THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

THE ONE HUNDRED AND THIRD GENERAL MEETING of the Institution of Petroleum Technologists was held at the Royal Society of Arts, John Street, Adelphi, on Tuesday evening, October 11th, 1927, Dr. A. E. Dunstan occupying the Chair in the unavoidable absence of the President.

The Chairman reminded members that nominations for Council should be in his hands by the 31st January, 1928. He further announced that the Ninth Annual Dinner would be held at the Connaught Rooms on Tuesday, 6th December, 1927.

The Secretary read the following list of members who had been elected since the last meeting :—

The following gentlemen have been elected as :—

Members.—Alexander Frederick Brown, Raymond Godet, Oswald Hardy Griffiths, John Eric Haslam, Frederick Glenn Jackson, George S. Joannides, Edward Silvester Kerkhoven, Herschel Gaston Smith, Herman Lourens Van der Meer, Mario Luis Villa.

Members (Transferred).—William English, Henty Tatham.

Associate Members.—Charles Howard Alberding, Arthur Emilio Allen, Dennis Comins, Percival Charles Errey, William Hoffman Farrand, William John Harris, Laurence Henry Joseph Hersch, William Johnston, Hugh Vaughan Lavington, William Henry Lowe, Charles Edmund Massey, Reginald Pardoe Matthew, Andrew Morrison, Stewart Nicol, Robin Roy Redgrave, Edgar William Sheel, James Rintoul Smellie, Arthur Edward Southern, George Stevenson, Lew Suverkrop, Bernard Joseph Vavasour, Percy Vickers, Arthur Cecil Vivian, Arthur Oliver Westwood, George Herbert Willock.

Transfers to Associate Members.—Percival Driver, Austin Lloyd, Douglas Rees, Harold Wallace Reid, William George Chealyn Tomalin.

Students.—Oswald Augustine Bell, Robert Henri Dewald (junior), Cyril George Digby, Archie Ronald Javes, William Alexander Hugh Oswald.

Associates.—Gordon Martin Ellis, Robert Desmond Forrester, Thomas Traill MacLean, Donald Simmons.

The Chairman said he had the greatest pleasure in calling upon Mr. Horace Young to read his paper, for two very different

reasons. In the first place, many more years ago than either of them cared to remember, he had the opportunity of instructing Mr. Young in the fundamental principles of chemical investigation, and he was sure Mr. Young had not forgotten the precepts laid down after that long lapse of time. The second, and the more particular reason, was that the paper which Mr. Young was about to read put forward the consumer's point of view. It was very important indeed for the Institution, which was comprised mainly of producers, to realise at times that the consumer existed, and that he had complaints and difficulties for which it was desirable that remedies should be found. Possibly one reason why this country had lagged behind other countries in industrial progress was that sufficient cognisance had never been taken of the difficulties of the consumer. The manufacturer of any particular article too often assumed the "Take it or leave it" attitude.

The following paper was then read:—

"Corrosion by Oil."

By Horace J. Young, F.I.C. (Member).

Severe corrosion having occurred on the pins and journals of the crankshafts of two motor ships it fell to the author to ascertain the cause and, if possible, to find a remedy. Fig. 1 is one of the corroded pins, which photograph is typical of all the pins and journals. Fig. 2 shows the corroded white metal in the bearings.

For obvious reasons the author cannot dwell upon the problem as it affected his clients' business. Sufficient to say that never before, in the author's experience, has applied science been so able to demonstrate to the satisfaction of the practical engineer exactly how his troubles arose. This paper, therefore, is confined to a description of the work done and is presented in the belief that it will throw some new light upon corrosion by oil, and perhaps establish some improved methods of testing oils for corrosive properties.

It is vital to this paper to state that the oils, as taken from the lubrication systems of the ships, were fully examined by, at least, two competent and independent laboratories and were reported to be innocent of causing the corrosion. Moreover, the laboratories in question knew of the trouble which had occurred and their work was directed with that in view.

As the result, however, of many hours spent on the engines concerned, the visual inspection of the working parts of those

* Paper received September 3rd, 1927.

engines and the analysis of a large number of samples collected during that examination, the author was led into a new train of thought from which arose directly and simply the solution of the mystery.

The position at that time was that corrosion had happened—corrosion of the most virulent and destructive type—in spite of which, tests of the oils gave no clue to the cause of the trouble. All other explanations being hypothetical and unacceptable to the author, he arrived at the conclusion that the analyses must be valueless and devised, what he calls, a Direct Oil-Corrosion test (for the sake of brevity, this test in future will be referred to as the D.O.C. test).

The test is performed by means of an apparatus whereby warm oil is run continuously over warm steel, white metal, brass, copper, or any other metal. The temperature employed by the author was 10° C. below the boiling point of water, but may be any temperature demanded in any particular case. In order to reproduce the conditions of the pins and journals, slabs were cut from similar steel and one-half of their surfaces "white-metalled" with bearing metal of the same make and quality as that used on the engines. It was possible, therefore, in one and the same test, to observe the effects of the oil upon the steel, the bearing metal, and at the point where the two materials met—as a matter of fact, over many experiments, there has been no definite indication of increased activity at this junction.

The original apparatus, namely, the first one made, is shown in Fig. 3. The aspirator bottle contains the oil-sample which flows down and through the U-tube and out at the glass-jet—the rate of flow being controlled by a screw clip. The U-tube is immersed in a tank, containing water or other suitable liquid, heated by a burner underneath. A triangular bar is attached to the side of the tank and attains its temperature. Studs are inserted at definite intervals into the triangular bar by means of which the specimens, when laid upon it, are kept in position and prevented from slipping off. The whole arrangement is seen in Figs. 3 and 4.

The first test of this nature, when applied to the oils from the two motor ships, showed immediately that they were highly corrosive to both steel and white metal. This aspect of the problem was nothing less than astounding, the new position being as follows :—

(1) The immense damage on these two ships had been caused by the oils.
(2) The analysis of the oils had shown nothing.

(3) Direct means had been found of proving whether an oil is corrosive.

(4) Hence, it might well be possible to find a cure for the trouble.

The D.O.C. test justified these hopes. Fig. 5 depicts a large apparatus testing samples of oil from many different sources. Here, twenty-five samples at a time can be tested, one operator only being required. The aspirator-bottles usually contain 250 c.c. of sample, but for cleaning or other tests bottles of 1000 c.c.

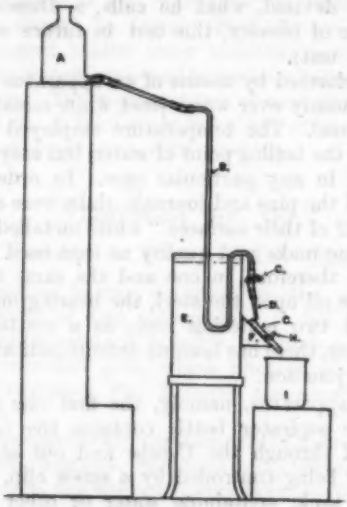

FIG. 4.

D.O.C. TEST APPARATUS.

End elevation. This apparatus is of sufficient size to carry out five tests at the same time, using one Bunsen burner under the bath.

A. Aspirator, 250-1000 c.c. capacity.
B. Glass tubing, 3/16"—¼" external diameter.
C. Screw clip.
D. Glass jet.
E. Bath, 4½" x 8" x 18" long.
F. Triangular bar.
G. Specimen, 2" x 2" x ¼".
H. Stud.
I. Beaker, 250-1000 c.c. capacity.

capacity are used. Messrs. Brady & Martin, Ltd., the scientific-instrument makers, of Northumberland Road, Newcastle-on-Tyne, have undertaken the manufacture of this apparatus, in any size and for any number of tests, for the use of laboratories and testing departments.

After considerable experiment it was discovered that the steel or other specimen should be polished to that degree produced

by No. 0 Emery—under the microscope, at 50 diameters, the steel appears as in Fig. 6 and the white metal as in Fig. 7. Although, as seen in later photographs, visual examination provides sufficient proof whether an oil is safe to use, the action may be studied more scientifically and accurately by the aid of the microscope at a magnification of 50 diameters. The following photographs, Figs. 8 to 19, taken at this magnification, are typical of the effects obtained.

Ordinary photographs of the above specimens, taken full size, show their appearance to the naked eye. These are given in Figs. 20–25. It will be observed that the final condition of the specimens depends upon the kind of contamination present in the oil and to no small degree can a skilled observer detect these effects.

Before leaving this interesting point regarding the appearance of the specimens the author presents some further photographs as follows :—Figs. 26, 27 and 28 : Action of system-oils from several motor ships, which oils were corrosive ; Figs. 29 and 30 : Action of similar oils from other ships, which oils were slightly corrosive ; Figs. 31 and 32 : Action of two oils from the sumps of motor cars ; mileage uncertain but under 5000.

In the case of oils from internal combustion engines of all types it would appear that the corrosive deterioration or the contamination is accumulative. For this reason the specimens from the D.O.C. test need to be examined under a microscope. This side of the work is yet in progress and little can be said beyond stating that it has been proved that many of such oils are corrosive, to a greater or lesser extent, to steel, white metal and so on. The gravity of this state of things, from a practical point-of-view, is evident. It may be true—in certain cases it certainly is true—to say that some of the effects ascribed to attrition are due directly or indirectly to corrosion by oil.

Analysis having failed to detect the properties of oils which D.O.C. tests proved to be highly corrosive, it appeared necessary to conduct a research upon an oil to which definite quantities of acid had been added. A lubricating oil (A) giving negative results under the D.O.C. test was chosen. This oil has the following analysis :—

Closed flash point	297° F.
Specific gravity at 70° F.	0·8893
Redwood viscosity at 70° F.	1047 secs.
Acid value	0·08%
Saponification number	0·20%
Inorganic acid (I.P.T., L.O. 5)	Nil.
Ash	0·002%
Total sulphur	0·229%
Water	under 0·05%

To this was added known amounts of concentrated sulphuric acid and the inorganic acid test (I.P.T.) again applied. The results are as follows:—

	Sulphuric acid added. % SO_4.	Inorganic I.P.T., L.O. 5. %	Sulphate value. % SO_4.
Original oil A			
(1) " plus acid ..	0·1883	0·017	0·111
(2) " " ..	0·0188	—	0·007
(3) " " ..	0·0019	—	0·0005

(*Note.*—The sulphate value is in accordance with the analytical method described in the appendix.)

Sulphuric acid to the amount of 0·1883 per cent. SO_4 was added to two other Oils of the following analyses, both oils being non-corrosive under the D.O.C. test.

	Mineral bearing oil (B). %		Compressor compound oil (C). %
Acid value	0·07	..	0·05
Saponification number	Nil.	..	1·01
Inorganic acid (I.P.T., L.O. 5)	Nil.	..	Nil.
Ash	0·014	..	Nil.
Total sulphur	0·722	..	0·690
Water .. .. under	0·05	under	0·05

When analysed, these gave:—

	Sulphuric acid added. % SO_4.	Inorganic acid I.P.T., L.O. 5. %	Sulphate value. %
(4) Original oil B, plus acid ..	0·1883	0·089	0·126
(5) " C, " ..	0·1883	0·017	0·164

Thus the Inorganic Mineral Acid estimation appeared to be valueless; throughout these investigations it gave negative results upon service oils, which the D.O.C. test showed to be highly corrosive and which had a high sulphate value.

The above five "acidified" oils gave the following results on the D.O.C. test:—

Sample.	Sulphuric acid added. % SO_4.	Volume of oil employed. c.c.	Total volume passed over specimen. Litres.	Number of heatings.	Total hours of heating.
Oil A (1) ..	0·1883	250	4·2	6	32
" A (2) ..	0·0188	"	4·2	6	32
" A (3) ..	0·0019	"	4·2	6	32
" B (4) ..	0·1883	"	3·8	8	47½
" C (5) ..	0·1883	"	3·8	8	47½

Result of Test.

Sample.	Steel.	White metal.
Oil A (1) ..	Very bad attack	Very bad attack, removed in places
„ A (2) ..	Slight etching	Darkened
„ A (3) ..	Slight etching	Untouched
„ B (4) ..	Very bad attack	Very bad attack, removed in places
„ C (5) ..	Very deep attack	Removed in oil path

In the case of acidified oils No. 2 and 3 the test was continued :—

Sample.	Total volume passed over specimen. (Litres.)	Total number of heatings.	Total hours of heating.
Oil A (2)	16·2	19	111½
„ A (3)	16·2	19	111½

Result of Test.

Sample.	Steel.	White Metal.
Oil A (2) ..	Serious effect	Being attacked
„ A (3) ..	Slight but definite etching	Darkened

This proved that 0·1883 per cent. SO_4 (added as H_2SO_4) is fatal in 32 hours, whilst one-tenth of that amount, namely, 0·0188 per cent., has a serious effect in 111 hours; while one-hundredth, namely, 0·0019 per cent. is beginning to make a definite attack after 111 hours. It is to be remembered, when considering the results, that only 250 cm.^{3} of the "acidified" oil was employed in each test and that the result might be expected to have been worse had, say, 16 litres been used.

The D.O.C. test was repeated on "acidified' oils 1, 4 and 5 with the sole difference that 10 per cent. by volume of water was added. After 47½ hours heating, the attack upon both steel and white metal was found to be very severe; if anything, slightly worse than when no water was present.

The original oil A, which was non-corrosive to steel or white metal by the D.O.C. test, was digested with potassium hydroxide solution and thoroughly washed. This is called sample (6). Another sample was prepared by adding 50 c.c. of sea-water to 50 c.c. of the orignal oil A, evaporating off all aqueous matter, adding 200 c.c. of the original oil A, and heating to 80° C. for half-an-hour. This is called sample (7). Under the D.O.C. test were obtained the following results :—

Sample.	Total volume passed over specimen. (Litres.)	Total number of heatings.	Total hours of heating.	*Result of Test.* Steel.	White metal.
Oil A (6) ..	16·2	19	111½	Slight action.	Darkened and corroded.
„ A (7) ..	9·6	14	79½	Pitted (not etched) particularly where jet touches	Pitted

Analysis of the sea-water (of which 50 c.c. was added to sample (7)) showed:—

	Grains per gall.
Total solids at 105° C.	2657·6
„ at dull red heat	2328·6
„ sulphates	165·2
„ chlorides	1360·6

At the conclusion of the test of sample 6, the oil was analysed for water and found to contain less than 0·05 per cent.

It appears that caustic treatment of an uncorrosive oil causes it to become corrosive in spite of washing the oil to remove the caustic. Also sample (6) proved that the D.O.C. test is sensitive to a small amount of sea water salts and that the effects upon the steel and white metal are of a different character to those produced by oils contaminated by sulphuric acid, sulphates or products of combustion.

Better to observe the effects of cleaning "acidified" oils by means of various reagents, the following tests of cleaned oils were made on the D.O.C. apparatus, 250 c.c. of oil being used for each test, the oil being heated with the cleaning reagent for three hours. The KOH solution contained 210 grams in 300 c.c. water

Sample.	Sulphuric acid added. % SO_4.	Cleaning reagent used. c.c.	Number of washings.	Subsequent treatment.
Oil A (1)	0·1883	50 KOH	3	None
„ (2)	0·0188	„	3	„
„ (3)	0·0019	„	3	„
„ (8)	0·1883	„	3	Al in excess
„ (9)	„	40 KOH	4	None
„ (10)	„	50 „	1	„
„ (11)	„	50 (double-strength)	3	„
„ (12)	„	50 KOH + 15 NaSilicate	3	„
„ (13)	„	50 NaOH	3	„
„ (14)	„	Nil.	3	„
„ (15)	„	Nil.	3	Al in excess plus 12·5 cm.³ water

FIG. 1.

CORROSION ON PIN OF CRANKSHAFT.

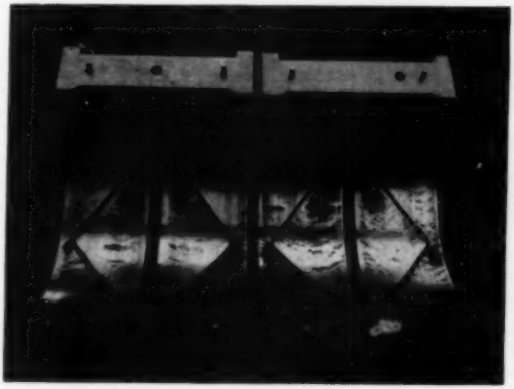

FIG. 2.

CORROSION ON WHITE-METALLED BEARINGS.

FIG. 3.
ORIGINAL D.O.C. TEST APPARATUS.

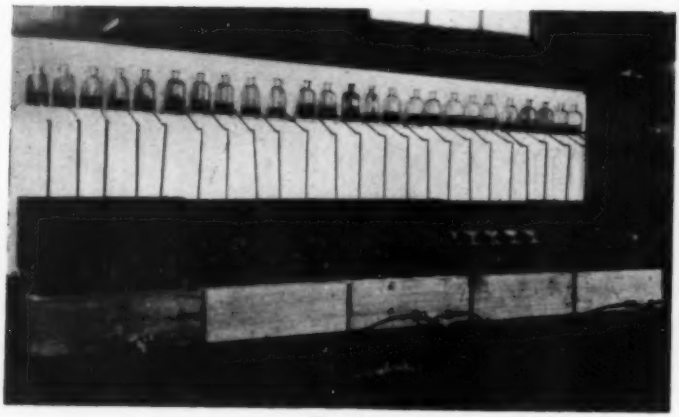

FIG. 5.
PRESENT D.O.C. TEST APPARATUS.

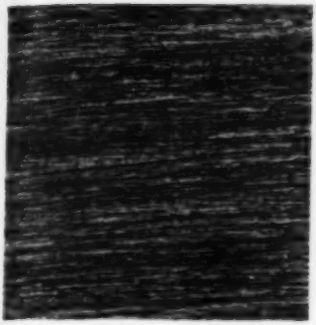

FIG. 6. STEEL SPECIMEN, POLISHED WITH NO. 0 EMERY.

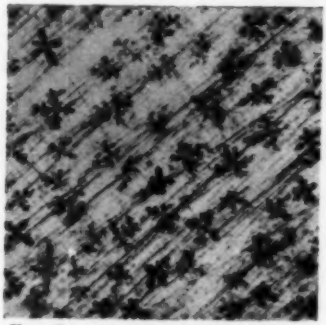

FIG. 7. WHITE-METALLED PORTION OF STEEL SPECIMEN, POLISHED WITH NO. 0 EMERY.

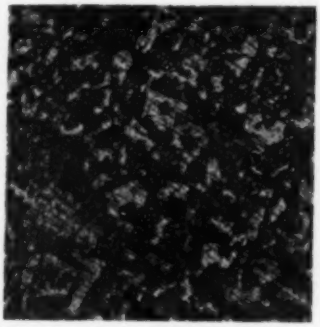

FIG. 8. STEEL SPECIMEN ETCHED BY OIL FROM MOTOR-LORRY.

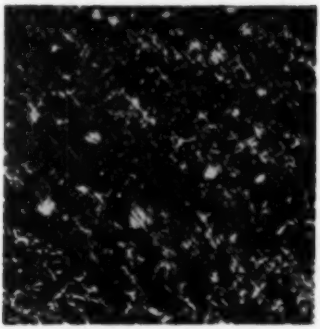

FIG. 9. WHITE METALLED PORTION OF STEEL SPECIMEN (FIG. 8) ETCHED BY OIL FROM MOTOR-LORRY.

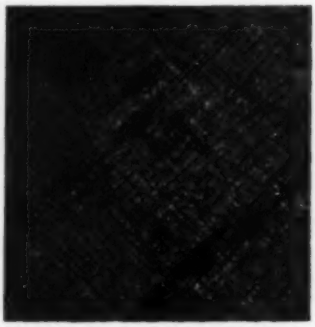

FIG. 10. STEEL ETCHED AND ATTACKED BY OIL FROM SYSTEM OF MOTOR-SHIP.

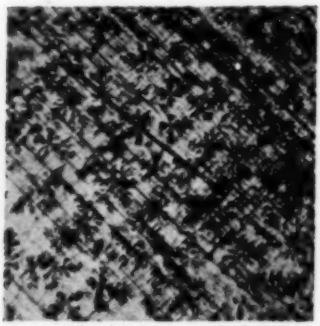

FIG. 11. WHITE-METALLED PORTION OF STEEL SPECIMEN (FIG. 10) ETCHED AND ATTACKED BY THE OIL.

MAGNIFICATIONS : × 50.

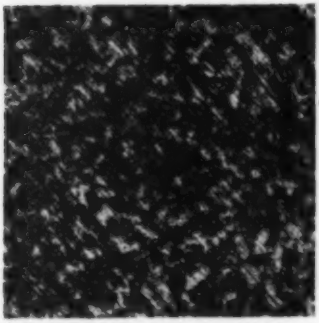

FIG. 12. STEEL (IN CENTRE OF OIL FLOW) ETCHED AND ATTACKED BY OIL FROM ANOTHER MOTOR-SHIP.

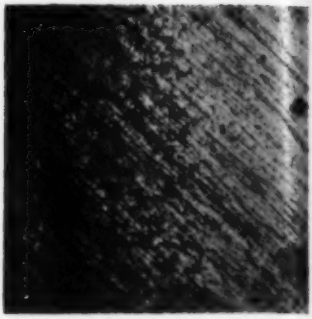

FIG. 13. SAME AS FIG. 12, BUT SHOWING ATTACKED AND UNATTACKED STEEL AT EDGE OF OIL FLOW.

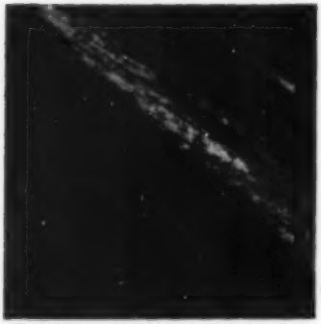

FIG. 14. WHITE-METALLED PORTION OF STEEL SPECIMEN (FIGS. 12 AND 13) ATTACKED AND REMOVED BY THE OIL.

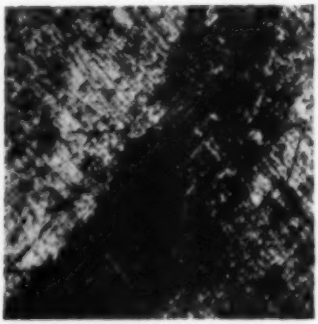

FIG. 15. WHITE-METALLED PORTION OF STEEL SPECIMEN ATTACKED AND REMOVED BY MOTOR-SHIP'S OIL *after* THAT OIL HAD BEEN TREATED WITH Na_2CO_3 SOLUTION AND WASHED.

FIG. 16. STEEL ETCHED AND ATTACKED BY MOTOR-SHIP'S OIL *after* THAT OIL HAD BEEN TREATED WITH KDH SOLUTION, WASHED AND TREATED WITH Al.

FIG. 17. WHITE-METALLED PORTION OF STEEL SPECIMEN (FIG. 16) ATTACKED AND LARGELY REMOVED BY THE OIL.

MAGNIFICATION : × 50.

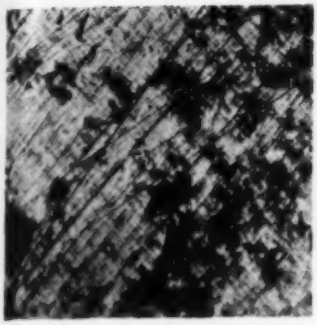

FIG. 18. STEEL SPECIMEN ETCHED AND ATTACKED BY UNUSED OIL CONTAINING SEA-WATER SALTS.

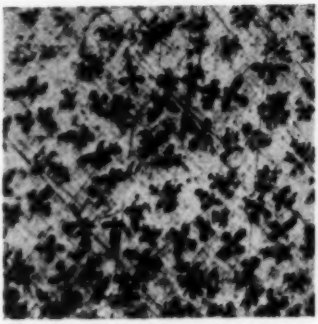

FIG. 19. WHITE-METALLED PORTION OF STEEL SPECIMEN (FIG. 18) ETCHED BY THE OIL.

Magnification × 50.

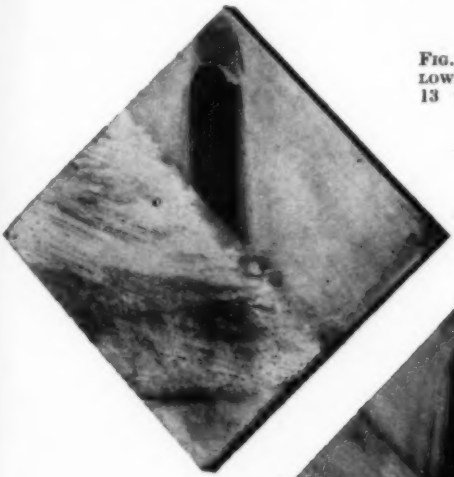

FIG. 20 (SEE FIGS. 8 AND 9). LOWER PORTION OF SPECIMEN 13 WHITE-METALLED IN ALL CASES.

FIG. 21 (SEE FIGS. 10 AND 11).

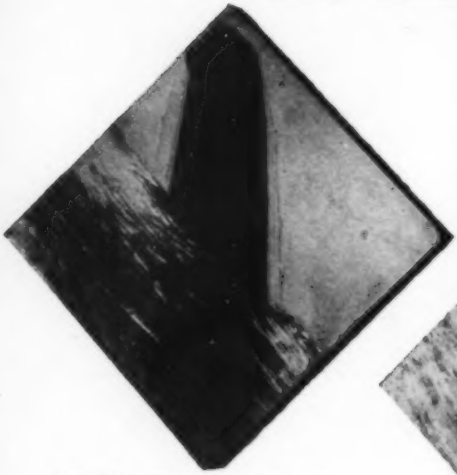

FIG. 22 (SEE FIGS 12 AND 14).

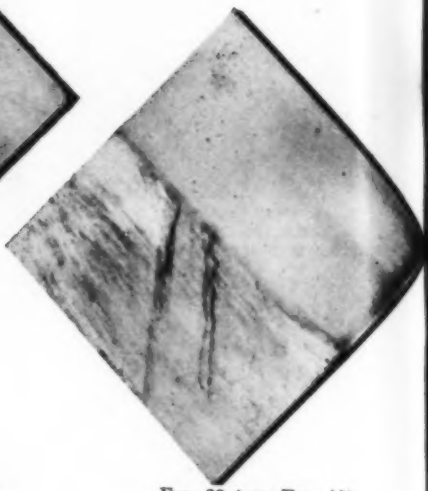

FIG. 23 (SEE FIG. 15).

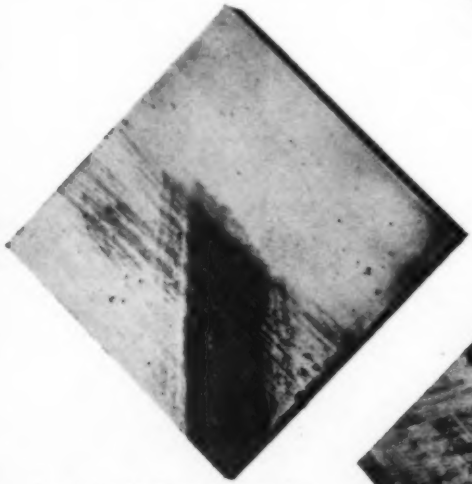

FIG. 24 (SEE FIGS. 16 AND 17).

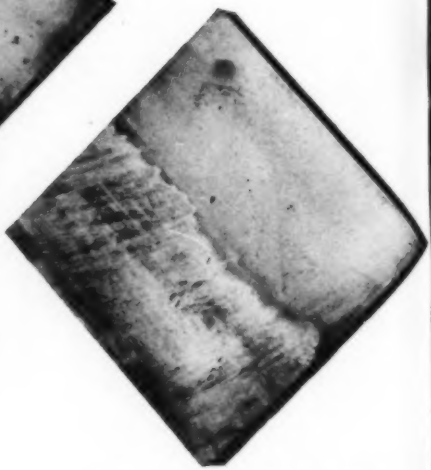

FIG. 25 (SEE FIGS. 18 AND 19).

FIG. 26.
MOTOR-SHIP'S OIL, VERY CORROSIVE.

FIG. 27.
MOTOR-SHIP'S OIL, VERY CORROSIVE.

FIG. 28.
MOTOR-SHIP'S OIL, VERY CORROSIVE.

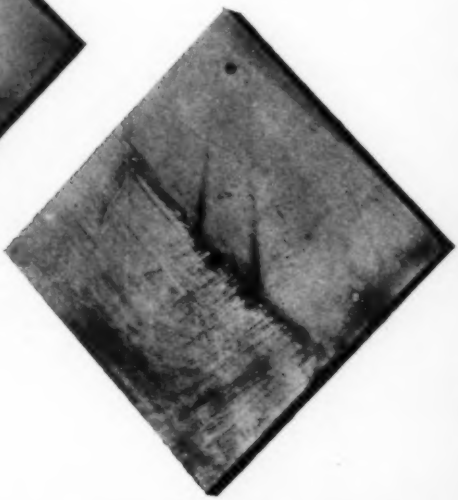

FIG. 29.
MOTOR-SHIP'S OIL, SLIGHTLY CORROSIVE.

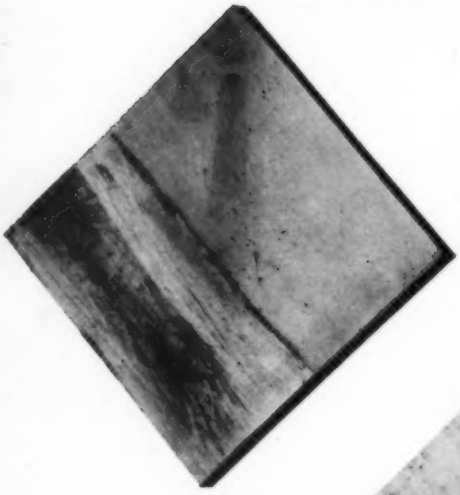

FIG. 30.
MOTOR-SHIP'S OIL, SLIGHTLY CORROSIVE.

FIG. 31.
MOTOR-CAR OIL. CORROSIVE.

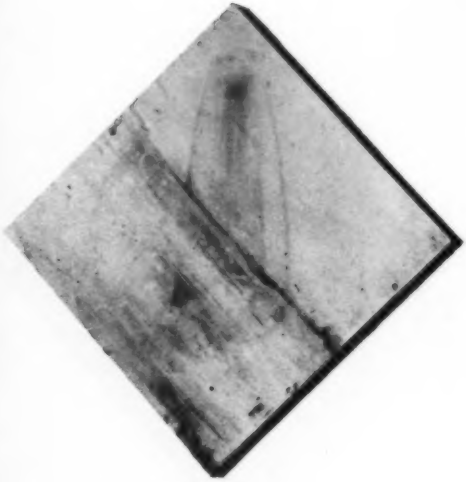

FIG. 32.
MOTOR-CAR OIL. CORROSIVE.

Sample.	Total vol. passed over specimen. Litres.	No. of heatings.	Total hours of heating.	*Result of Test.* Steel.	White metal.
(1)	16·2	19	111½ ..	Slight corrosion	Slight corrosion
(2)	16·2	19	111½ ..	„	„
(3)	16·2	19	111½ ..	Very slight corrosion	Darkened
(8)	3·8	8	47½ ..	Slight corrosion	Darkened and partly removed
(9)	3·8	8	47½ ..	Considerable etching	Darkened and coloured
(10)	8·4	15	85½ ..	No action	Darkened
(11)	8·4	15	85½ ..	Slight corrosion	Being removed
(12)	3·8	8	47½ ..	Pitted and etched	Coloured
(13)	8·4	15	85½ ..	No action	Darkened
(14)	8·4	15	85½ ..	Slight corrosion	Slightly darkened
(15)	8·4	15	85½ ..	Decided etching	Starting to be removed

It became evident from the above tests that, so far as practice is concerned, alkali treatment is unsuccessful for the reason that the alkali and salts cannot be removed completely by washing. Other alkalies, such as carbonate of soda, were tried with similar results. If the efficient washing possible in a laboratory is insufficient it would appear hopeless to expect good results from such washing as can be done in practice. That we have been unable previously to demonstrate these happenings has been due, the author believes, to the failure of chemical analysis as applied to such work and the lack of a direct method as is the D.O.C. test.

Reverting to those oils which become corrosive in service, many samples have been subjected to the D.O.C. test and have been analysed by the sulphate value method (given in appendix) as previously applied to the "acidified" samples. The results are of extreme interest. All the following oils have been taken from the lubrication systems of motor ships and are arranged in order of their sulphate values.

Sample.	Sulphate value % SO_4.	Vol. of oil employed. c.c.	Total vol. passed over specimen. Litres.	No. of heatings.	Total hours of heating.
(16) ..	0·2261	250	10·6	15	90½
(17) ..	0·1917	„	7·8	11	74½
(18) ..	0·1486	„	4·6	7	44
(19) ..	0·1456	„	3·8	6	36
(20) ..	0·0884	„	10·2	12	85½
(21) ..	0·0840	„	16·2	19	111½
(22) ..	0·0813	„	11	15	95½
(23) ..	0·0534	„	10	16	87½
(24) ..	0·0526	„	6·2	10	67½
(25) ..	0·0507	„	16	16	87½
(26) ..	0·0224	„	6	9	54½
(27) ..	0·0123	„	9·2	14	77½
(28) ..	0·0117	„	13·6	19	118½
(29) ..	0·0102	„	16·5	19	124

Result of Test.

Sample.	Steel.	White metal.
(16) ..	Very badly etched	Removed and the steel underneath badly etched
(17) ..	„	Completely removed
(18) ..	Considerable etching	Removed in parts
(19) ..	„	„
(20) ..	Considerable etching and pitting	Nearly completely removed
(21) ..	Badly pitted	Removed in parts
(22) ..	Considerable etching and pitting	Nearly completely removed
(23) ..	„	Being attacked
(24) ..	Pitted and beginning to etch	Pitting and deeply etched
(25) ..	„	Being attacked
(26) ..	Light etching and pitting	„
(27) ..	Considerable pitting and lightly etched	No action
(28) ..	No action	„
(29) ..	„	„

Thus it will be seen that a sulphate value of more than 0·05 per cent. is an indication that the oil is dangerous to use.

Corrosive powers are active down to as little as 0·012 per cent. sulphate value. It should be noted that all these oils were tested for inorganic acid (I.P.T., L.O. 5), the results showing either nothing at all or a trace too small to matter. A series of cleaning tests, somewhat similar to those described in the case of the "acidified" oils, were carried out on most of the above oils, many alkalies being tried together with other methods such as steam cleaning. Alkali treatment was unsuccessful by reason of the

impossibility of complete washing, whilst steam cleaning was marred by the difficulty of emulsions being formed unexpectedly and sometimes considerable losses of oil occurred before separation could be effected.

Experiments have been made, using the D.O.C. apparatus, with a view to finding out if the corrosive properties of an oil became exhausted as the result of running it over steel. The results have proved most conclusively that the vitality of the sample remains unabated and, after many hours' running, when the corroded piece of steel has been replaced by a fresh piece, the attack continues unaltered. Evidently the products of corrosion are as corrosive as the orignal corrodent—possibly in the case of an internal combustion engine there is at any time little difference between them. In using the sulphate value it is essential to know also the results of a D.O.C. test, because experiments have been made by adding sulphates to uncorrosive oil and it was found that all sulphates are not equally corrosive under these conditions.

It will be remembered that in the case of the " acidified " oils some of the added sulphuric acid could not be extracted by caustic potash. Yet this " lost " acid was harmless to steel. This phenomenon gave rise to much doubt when considering the early experiments, and steps were taken to ascertain whether at any period sulphur gases were evolved from the sample such as might account for the apparent " loss " of sulphuric acid. No evolution of any gases whatsoever was detected.

In practice, however, we are interested merely in those things which cause corrosion, and somewhat fortunately the "lost" acid does not.

Very much more work is needed upon this subject, and many points of interest have arisen in the course of this research.

Up to the time of writing, and speaking of many experiments, no new unused mineral or compound oil has corroded steel under the D.O.C. test; on the other hand, none of these same oils has not caused pitting or corrosion on copper and on brass.

A selection of some of the D.O.C. test results using copper or brass may be interesting :—

		Acid value. %	Saponification No. %
Sample D.	Used oil from system of motor ship.		
„ E.	„ „ „ another ship.		
„ F.	Unused oil	Nil.	0·20
„ G.	„ compound oil	0·05	1·01
„ H.	„ oil	0·07	Nil.

These oils were tested using either copper or brass specimens.

Sample.	Vol. of oil employed. c.c.	Vol. passed over specimen. (Litres).	No. of heatings.	Total hours of heating.	*Result of Test.*
Sample D ..	250	4·8	8	43½	Brass pitted and etched
„ D ..	„	„	„	„	Copper „ „
„ E ..	„	„	„	„	Brass „ „
„ E ..	„	„	„	„	Copper „ „
„ F ..	„	11·2	15	99	Copper more pitted than etched
„ G ..	„	8·8	7	45	Copper pitted and marked
„ H ..	„	8·6	7	45½	Copper very slightly marked

SUMMARY.

By the D.O.C. test as little as 0·002 per cent. H_2SO_4 can be detected, and the test is equally sensitive to minute amounts of sea-water, alkalis, sulphates and so on. The alkalis so readily affect white metal that an oil cleaned by alkali will attack white metal even when that oil has been washed three or four times with water.

The D.O.C. test thus affords a means of testing the efficiency of any cleaning process. In this connection it has led to the perfecting of a simple appliance which, inserted into an oil-system, will keep the oil "sweet."

The study of compound lubricants as used on compressors is greatly facilitated and, at the time of writing, valuable information is being obtained as to the effects of high acid value (oleic), high saponification number and so on.

In practice the D.O.C. test is being used as a means of watching the oils on internal combustion engines for land or marine work, and within a few hours of receiving the sample it is possible to tell the owners whether their oil is becoming dangerous to use. In transport work—automobiles, lorries, motor buses—great interest has been shown in this matter, many oils being found to be corrosive. In another direction, an expert marine engineer has expressed the opinion that the D.O.C. test may throw light upon the pitting of the teeth of turbine gearing which sometimes takes place in a manner never satisfactorily explained.

Corrosion in pipe-lines is not unknown, and the work of discovering its progress, cure or prevention may be facilitated by this test.

The author feels that no apology is needed for thus advocating a test which during the past twelve months has proved invaluable to him in his practice and in which practical men connected with

many different branches of engineering are expressing the highest interest.

In conclusion he desires to say that much of the work has been carried out by his head-assistant, Mr. H. C. Jay, whose skill and advice have proved invaluable in bringing the test to its present position of utility.

Also he expresses his thanks to Messrs. Swan, Hunter & Wigham Richardson, Ltd., Neptune Works, Newcastle-on-Tyne, where the original work was done and where the importance of the results was recognised and made use of. Not less has he appreciated the kindness and interest of others who have sent in authentic samples. The omission of many results is due solely to the need of keeping this paper within reasonable limits.

APPENDIX.

Sulphate Value Test.

(1) $\frac{1}{4}$100 c.c. sample in 600 c.c. beaker. Add 20 c.c. KOH solution (210 grams in 300 c.c. H_2O). Keep at just below 100° C. for 3 hours with air bubbling through meanwhile.

Add 90 c.c. hot water. Transfer to 500 c.c. separating funnel and shake vigorously. When separated, tap off 70 c.c. of the alkaline solution into a 200 c.c. beaker, acidify with 20 c.c. strong HCl, boil, filter and treat with $BaCl_2$ in the usual manner. ($BaSO_4 \times 0{\cdot}411 = SO_4$.)

(2) An exhaustive examination of used oils from motor ships has been conducted on several occasions and the following example is given as containing details of considerable value. In the first place, there is the original unused oil, then the black used oil from the system and, finally, the residue from the latter and the oil freed from this residue.

	New unused oil.	Black used oil.	Same freed from residue.
Sp. gr. at 70° F.	0·8893	0·9157	0·8913
„ at 150° F.	0·8607	0·8881	0·8633
Viscosity at 70° F.	1046 secs.	2557 secs.	910 secs.
„ 90° F.	517 „	1261 „	498 „
„ 110° F.	276 „	673 „	272 „
„ 130° F.	166 „	383 „	174 „
„ 150° F.	110 „	250 „	123 „
Acid value	0·08%	0·13%	0·8%
Saponification number	0·20%	0·42%	0·26%
Inorganic acid (I.P.T., L.O. 5) ..	Nil.	Nil.	Nil.
Sulphate value	—	0·0840%	0·0129%
Ash	0·002%	0·353%	0·029%
Copper in ash	Nil.	Trace	—
Total sulphur	0·229%	0·225%	—
Water .. .. .. under	0·05%	18·4%	—
Residue insoluble in benzene ..	—	1·52%	—

ANALYSIS OF RESIDUE.

	per cent.
Moisture (H_2O)	5·44
Silica (SiO_2)	N l.
Iron oxide (Fe_2O_3)	11·30
Aluminium oxide (Al_2O_3)	0·90
Copper oxide (CuO)	0·30
Carbon (C)	52·8
Lime (CaO)	0·47
Magnesia (MgO)	1·28
Soda (NaO)	4·52
Sulphate (SO_3)	6·31
Chloride (Cl)	8·13

A water extract of this residue gave the following analysis:—

	per cent.
Magnesia (MgO)	1·28
Soda (Na_2O)	4·52
Sulphate (SO_3)	2·49
Chloride (Cl)	8·13
Alumina (Al_2O_3)	0·50
Acidity	0·77

DISCUSSION.

The Chairman said that before throwing the paper open for discussion there were a few points he desired to put to the author. In the first place, only a short time ago a case occurred upon which the paper threw very considerable light. It referred to an 8-cylinder Diesel ship, in four cylinders of which very much more wear was experienced than would be anticipated normally. On the four other cylinders normal wear only took place. The theory put forward by the manufacturers of the engines was that the fuel burned in the engines was sulphurous, and that the products of combustion had corroded the engines. If that theory was correct there was no reason why the eight cylinders should not have been corroded. After reading the paper it occurred to him that the cause of the wear might be corrosion due to the lubricating oil. He desired at an early point of the discussion to ask the author whether he was certain that the sulphate values to which he ascribed corrosion were inherent to the oil or adventitious to the oil. It appeared incredible to him that the normal sulphur content of a lubricating oil, which was frequently much more stable than the hydrocarbons associated with it, should break down in some mysterious form and form acid that was corrosive. Looking at the last analysis given, he felt rather inclined to think that it was the products of combustion that were the culprits, either carbonic acid, sulphuric acid or sulphurous acid dissolved in or emulsified in the oil. The point on which he desired the author to assure him was whether or not the oils for the tests were thoroughly dry before the tests were made.

Dr. W. R. Ormandy said the Chairman in his opening remarks made a statement which he thought those of the members who were connected with the sale of lubricating oil would hardly agree with—namely, that the people who used the oils did not bring their troubles to the notice of the manufacturer. He was under the impression that if anything went wrong in a works the man who sold the lubricating oil was the first person blamed, but apparently he was wrong: things had changed. He thought the members were very much indebted to the author for bringing before their notice a subject which would be provocative of considerable discussion and which would certainly open out a wide sphere of new research work. He desired to ask the author if the implication of his paper was that oils as sold contained in fact large quantities of sulphuric acid, combined more or less as sulphonic acids of various types, and that they were not amenable to extraction by means of the ordinary caustic soda test which was employed to ascertain whether acids were present, but that they were set free by the effect of air in the presence possibly of moisture. Did the author mean to imply that a certain amount of the sulphuric acid was so tightly combined that it was not even set free by heating to 100° C. with very strong caustic potash. If the claims the author made were in fact true they had a serious bearing on the whole of the oil industry. The bulk of the refining of the oils of the world was done by means of sulphuric acid and by washing subsequently with caustic soda; and the author stated that the washing with soda did not remove the sulphuric acid and that the washing by water did not remove the soda. The whole principle of refining as carried out at the present time was therefore absolutely brought into discredit if the interpretation of the results brought forward were those claimed by the author. That was an exceedingly serious statement to make, but nevertheless a great deal of weight must be attached to the fact that the author found some proportional connection between the amount of his sulphuric acid value and the amount of the corrosion that took place. What he could not understand, however, was that in spite of the fact that 26 or 27 million motor cars were running on the roads with white metal big ends for the most part, and polished steel crank pins, comparatively little was heard of the corrosion of crank pins and the removal of white metal from the bearings, because the lubricating oil, under the condition existing in a motor car crank case, was about as ideally situated as anything could be for the development of that corrosive action—i.e., the oil was at a temperature up to 80 or 90° and a good current of air was going through. Under those circumstances the astonishing thing was that there were any white metal bearings left at all, and he therefore

asked the author the question whether he had had any considerable complaints in regard to the corrosion of white metal and steel in motor car engines. An engineer, responsible for the running of very large numbers of motor cars all over the country, told him that it was a most exceptional thing to get obvious corrosion, either of the white metal or of the pins on which the white metal ran, and it was a strange thing that under such ideal conditions greater damage was not found. He desired to suggest to the author that the adoption of an accurate method for the determination of the free sulphur might lead possibly to another interpretation than the one he had given.

Engineer-Captain W. G. Heppel, R.N., said that when coal was used for the fuelling of the ships, large quantities of ashes had to be thrown over the side, and it was the practice never to do so while the main circulators were running, unless the ship was under way, mainly because the ashes were sucked through into the condenser tubes, causing considerable trouble. Incidentally another cause of trouble was that a certain quantity of ash got into the water service to the bearings. Eventually it drifted into the bearings themselves and produced a black deposit on the journals and the brasses. Great care was then exercised not to allow ashes to be thrown overboard at any time when any suction was going on in the ship, and all water that could possibly get to the journals and bearings was trapped in a fine gauze. Nevertheless the black deposit was still found, and it was put down for years to the presence of the ash. Eventually ships changed from coal burning to oil burning, and instances occurred of the black deposit on journals which could not possibly be attributed to the ash. Certain control gear, mainly pull and push, which was lubricated with mineral oil, and only used intermittently, jammed after a very short stay at sea, sometimes with serious results. A black deposit was found on the pins, although when the ship left port, two or three days before, they were perfectly clean. The trouble was put down in that case to a mixture of mineral oil and sea water. Eventually the engineers insisted on olive oil only being used for those particular rods, and that remedied the trouble. The author used the word "attrition" in the course of the paper, which was exactly what he (the speaker) meant in connection with the trouble found with the ashes, or with the black deposit and pitting caused apparently by the oil. He desired to ask the author what was the effect of using paraffin to wash out the engine of a motor car. Would it make things worse or better? In the case of an all-round movement a good deal of the harm which would be caused by any form of corrosion was washed out by the movement, provided engines

were used daily, but that was not the case with a crosshead journal in which there was only a partial movement. The worst conditions existed in a push and pull movement, such as a signal, which was only used occasionally, especially when it was subjected to sea water or sea atmosphere.

Mr. E. Lawson Lomax said there were a few questions he desired to ask in connection with the author's interesting paper. In the first place were all the oils on which tests had been carried out oils that had been used, or had some of the tests been done on fresh oils, and then again on oils which had been used? He asked that question because in the internal combustion engine, particularly of the Diesel type, about a hundred times as much fuel oil was used as any other oil during the course of the run, which fuel oils contained a large amount of sulphur, not sulphuric acid but various sulphur compounds, which might be neutral and would not give any reaction to the I.P.T. Acid Test. If the piston rings of the engines were not a good fit that was a possible passage both for unused oil or partly burned oil and the products of combustion into the sump containing the lubricating oil. In that case it would be possible easily to account for the increase in corrosion by use of the oil. He put that forward as it was a point which the author might not have thought of. In the next place the author, during his tests, added a certain proportion of acid to the oil, heated it, and then tested it afterwards. He desired to ask whether the acid was added to fresh oil in every case or to used oil, and also what was the strength of the acid that was added. It was known that a certain amount of decomposition of lubricating oils took place during use and also that sulphuric acid of a certain strength would form certain compounds with these oils which themselves would not give the acid reaction to the standard test. It was quite possible that the author had not been able to find all the acid owing to the fact that he had not used methods for decomposing these compounds or had not carried his tests far enough to ensure complete decomposition. Further, the author had made rather a peculiar statement in regard to the caustic soda cleaning. Personally he was afraid the manufacturer of lubricating oil would be in great trouble all the time if he left in sufficient caustic soda to cause corrosion in the oil. He thought if the author persevered with his washing he would be able to eliminate the caustic soda or to leave so little of it in that it would not cause any difficulty with regard to corrosion. The author also mentioned that he had never found a new oil that would corrode steel or white metal, but that most of such oils would corrode copper and bronze. It was pretty well known that copper and bronze were corroded by sulphur

compounds which had very little action on steel or white metal, and it was quite possible that that might be an explanation of what the author had found and which he attributed to the method of refining the oil.

Dr. F. B. Thole considered that Mr. Young had expressed some of his conclusions somewhat prematurely in view of the fact that several of the important factors involved in the corrosion had only been superficially studied. The author had stated that in a series of oils tested the order of increasing corrosiveness was approximately the same as the order of increasing "sulphate value," that is, to the amount of sulphate produced by heating the oil with caustic alkali under conditions similar to those employed in the estimation of "saponification value."

There were notable discrepancies which needed further examination. Thus with two oils of practically identical sulphate value (0·0123 and 0·0117) the former caused considerable pitting in steel while the latter after a much more prolonged corrosion test gave no corrosion.

The speaker suggested that perhaps "sulphates" were not the main cause of the corrosion and that arrangement of the oils in order of "chloride" value or "magnesium" value might have shown a better parallelism with corrosive action in view of the well-known corrosive action of moisture and sea salt, both of which were presumably present in most of the samples tested.

The ascription of corrosiveness to sulphates in general appeared still less convincing in the absence of specific evidence as to whether sulphates such as sodium or calcium sulphates were corrosive or whether only a few (such, for example, as the particularly hydroscopic ones) showed this property.

Mr. Young appeared to be surprised that, when sulphuric acid was added to an oil, the whole of this acid could not be accounted for by the I.P.T. determination of free inorganic acid, and states that "thus the inorganic mineral acid estimation appeared to be valueless." It is well known that when sulphuric acid is added to oil most of it enters into chemical reactions with the formation of various organic acids (alkyl sulphuric acids and sulphonic acids) and neutral esters, products which are obviously not "inorganic mineral acid" and which the test I.P.T. L.O.5 is not intended to estimate. The fact that the "sulphate value" does not account for the whole of this added sulphuric acid is also to be expected, for while alkyl hydrogen sulphates and ultimately the more stable alkyl sulphates would be saponified to sulphuric acid in this test the true sulphonic acids would remain as sodium salts unaffected by barium chloride.

The author has brought forward a test which has the decided merit of indicating directly, rather than by an indirect method, the effect of a sample of oil on metals, and such a test should be of material value to manufacturers and consumers of lubricating oil. The same cannot, however, be said of the "sulphate value" test.

Mr. J. Calderwood said he was fortunate in having been associated with the author in some of his earlier tests, particularly in the examination and collection of samples. At the same time he carried out some chemical tests rather in parallel with those of the author, but only of a preliminary nature. He desired in the first place to answer a remark made by Dr. Thole, who, he thought, had quite missed the point of the author's condemnation of the standard test for mineral acid. The standard test was condemned because it was generally accepted as showing whether the oil would cause acid corrosion or not, and as such the author condemned it. He did not think the statement could be read into any remark made in the paper that the remainder of the acid was still in the form of free acid. He thought the standard test could be condemned still further. For example, in one case he took a sample of oil, mixed acid with it and then tested it by the standard test. It showed 0·08 per cent. Actually he had put 0·79 per cent. into the oil. He then repeated the standard test on the oil which was supposed to have been already tested, and he got another 0·08 per cent. He continued to repeat the test, and it took fifteen repetitions to show how much acid was still there in the form of free acid. After that only 0·54 per cent. was obtained, so that at least 0·25 had actually formed some compound with the oil. A point which was not brought out in the paper was the amount of acid which could be absorbed by the oil in that way. He found that it was at least 1·5 to 2 per cent., which was a very large amount. That meant that an oil tested in the ordinary way and showing no indication of free mineral acid could have 2 per cent. of acid contained in it in the form of those very corrosive compounds. Such an oil, as a matter of fact, was tested with a piece of steel wire which it completely dissolved in the course of four or five hours. There was one question he desired to ask the author. He had tried a test for the sulphate value rather on the lines the author suggested. It worked satisfactorily in one or two cases, but very often the only result obtained was an emulsion with which he could do nothing at all. As soon as he started to try to clean the oil with KOH a very strong emulsion formed which it was utterly impossible to separate out by any ordinary means. He found that even the

slightest trace of acid made the oil extremely liable to form very stable emulsions, and he would like to know whether, in his much wider experience, the author had found the same effect, and to the same extent. An omission from the paper in regard to which he thought the author might supply some information in his reply was the source from which the sulphates got into the lubricating oil. The author had only stated in the paper that he took lubricating oils and found that they contained highly corrosive sulphates. He had also shown by means of the lantern slides that the action by a sulphate of that type and the action by sea water or chlorides in the oil was so different that it could immediately be detected by inspection of the test piece. In the course of the collection of the samples he remembered distinct indications that, at the time when he was working with Mr. Young, the sulphates in the oil were certainly originally formed in the cylinder of the engine; in other words, that the lubricating oil samples taken close up to the cylinder were very much more corrosive than samples taken in the crank case, and that it was possible to trace by various indications the path of the corrosive substance from the combustion space to the crank case. He hoped that the author in his reply to the discussion would state his final conclusions on that point, particularly as to whether the cause of the corrosion was from the fuel oil or from the effect of the heat in the cylinder on the lubricating oil. So far as the fuel was concerned, one would say at first sight that if there were any sulphur in the fuel it would have that effect, but on thinking it over a little it was seen that that could not be the case. The sulphur was transformed in the cylinder into sulphur dioxide or sulphur trioxide which in the ordinary way would not attack the oil. It was known that differences existed in different fuels, and it was possible that in some fuels there was combined sulphur in such a form that some of it was deposited in the cylinder and attacked the lubricating oil. That in itself was a very important point, because if corrosive action was going on in the bearings it must be much more active in the cylinder liners and the piston rings. That, he thought, might account for some of the very inconsistent effects of cylinder wear. Very frequently the wear in one engine was many times greater than in another, although the lubricating oil, the fuel oil, the cast iron, and everything else were exactly similar in the two ships so far as could be determined by the present methods of chemical analysis. It was possible that in one case the fuel oil used had sulphur present in a form which started corrosion, which would account for the heavy wear in the cylinder. Another effect which he thought was very noticeable was that oil corrosion was particularly liable to occur when the oil was in a very thin

film either between two bearings under high pressure or spread over an open surface. He would like to know the author's opinion as to whether a thick or a thin film of oil was more liable to cause the corrosion.

Mr. E. R. Redgrove said that for over twenty years he had had to bear the brunt of many of the complaints visited by the consumer upon the producer and consequently cases of corrosion were by no means unknown to him. The cases which he had investigated in marine work led him to believe that the trouble was due to one or both of the following causes :—

(1) Chlorides which found their way into the lubricating system either from the intake air or from actual sea water leakage.

(2) Sulphur acids formed during the combustion of the fuel. Seldom, if ever, could corrosion be directly attributable to the lubricating oil and then only if it was totally unfitted for duties which it was expected to fulfil.

He would suggest that in the attempt to remove the sources of corrosion it would be advisable carefully and thoroughly to filter the intake air and the lubricating oil, also to pay more attention to the method of storing not only the lubricating oil but also the fuel oil on board ship. Further, as it had long been known that the metal copper was a very active catalyst of the decomposition of lubricating oil, it would be advisable to eliminate copper entirely from the lubricating system, including the oil coolers and the compressor intercoolers.

He would like to ask if the author could give further particulars of the oils mentioned in the paper. Were all the oils examined non-corrosive before use and were any non-corrosive after use ? It seemed essential to know the refining history of the various oils if progress was to be made in preventing the evil. He did not know if the author in making his tests, some of which ran for over 100 hours, took any precaution to protect the surface of the metals from atmospheric pollutions. Sulphur and carbonic acids always present in the atmosphere might have a considerable influence on the amount of corrosion that occurred.

As the result of research work which has been going on for several years, he has come to the conclusion that sulphur in oil *per se* was not at all deleterious. In the oxidation test some oils containing only 0·18 per cent. of sulphur showed greater decomposition than oils which contained over 1·0 per cent. of sulphur. It was necessary to realise that there was a great difference between the ways in which sulphur could be combined in the oil molecule. If present as an impurity, as for instance sulphonic acids resulting from imperfect refining, trouble was likely to occur, but if present

as a constituent of the molecule and firmly combined therein, he did not see why an oil molecule containing two or three sulphur atoms should not be quite as stable as one in which the chain, or ring, consisted entirely of carbon atoms.

Mr. E. C. Craven said he desired to make the suggestion that the whole of the author's results as far as the sulphur side of the problem was concerned were very simply explained by the theory to which Dr. Ormandy referred in the last sentence of his remarks—namely, that the whole cause of the trouble was free sulphur. Lubricating oils, whether new or old, contained more or less free sulphur. Oils in use in the crank case of a motor car or in a Diesel engine were subjected to the action of SO_3, which invariably gave rise to free sulphur, and oil treated with sulphuric acid always contained afterwards a greater or less amount of free sulphur. That was borne out by the fact that the order in which metals in the author's experiments were corroded was the same as the order of the corrosion of metals by motor fuel containing free sulphur. Copper was the easiest to attack; it blackened and scaled. Brass was the next easiest; it did not blacken, but was pitted and spotted. Steel was very little attacked by a small amount of free sulphur, and this again is in accordance with the action of the lubricating oils. Phosphor bronze was very resistant. He had tested lubricating oils in a phosphor-bronze cup, and after examining hundreds of samples in the course of five years not one positive result was obtained. A test had been published for free sulphur in lubricating oils, and it would be very interesting if the author would try that test with one or two oils and compare the results with his own tests. One point which required consideration was how corrosion occurred from the presence of free sulphur. He took it that metallic sulphides were formed, and these in the presence of air and moisture were converted to oxides, the sulphur being set free again, and so the corrosion went on continuously, the sulphur acting as an oxygen carrier. It was difficult to see how the author could ascribe the corrosion to sulphates since no sulphur trioxide was extracted by caustic potash. In the author's "sulphate" test it was likely that the sulphides, thiosulphates and the like, together with sulphonates extracted by caustic alkalies, were converted by the air blowing into sulphates and were then capable of being precipitated by barium chloride.

With respect to the retention of caustic soda by oils he suggested this might be explained by the formation of soaps not extracted by hot water, but which might be removed by filtration through fuller's earth.

There were one or two chemical questions he desired to ask. In

the first place he did not understand the quantities in the sulphate test. The author started with a certain amount of caustic, added 90 cc. of hot water and tapped off 70 cc. To what volume were the results calculated ?

In the analysis of the water soluble residue the water of crystallisation seemed to be strangely distributed. Sodium chloride which did not crystallise with water till below 0° C. was allotted $2H_2O$, whilst magnesium sulphate and calcium sulphate were not given any.

Mr. S. Bowman congratulated the author on his ingenious device for detecting the corrosive property of oils, and asked him if an immersion test would indicate the same effect as that given in the paper.

He considered that the determination of acidity in oils by the known methods was unsatisfactory, and an investigation on this subject showed that when working with synthetic mixtures of mineral oil and oleic acid only 50 per cent. of the latter was extracted with aqueous alcohol.

The main question that arose from the paper appeared to be whether corrosion was due to the deterioration of the oil itself or to impurities arising from contamination. An almost identical case to those referred to by the author came before his notice in connection with corrosion on a marine Diesel engine. The used oil was black and badly emulsified and apparently contained no inorganic acid, at least it was impossible to detect this by washing with water owing to the stable emulsion formed. Using a high-speed centrifuge he was, however, able to separate out some of the water, and this was found to be distinctly acidic with a normality of 0·04. Furthermore, the water was proved to be sea water. The explanation at the time seemed to be that the action of sea water on the metal had formed iron salts which would readily hydrolyse, forming mineral acids, which in a closed system would be cumulative, and so the viscous circle went on.

Until it was definitely known what was the actual cause of corrosion, whether it was due to contamination or not, he thought it hardly fair that the sulphate test described by the author was a true indication of the oil as a corrosive agent.

Mr. S. E. Bowrey said the author seemed to imply that the test for mineral acids was the only test hitherto used to decide whether oil was corrosive or not. He thought it desirable to point out that most oil workers had been in the habit of practising a direct oil corrosion test of one form or another, not perhaps so elaborate or so satisfactory as the author's, but still a direct test. He would ask the author whether he had compared the results

of his D.O.C. test with those obtained by partly immersing slips of metal in the oil in a beaker and heating it to 90° C. or 100° C. for a length of time. Such a method had been used for some time past and was capable of revealing corrosive tendencies not brought to light by the mineral acidity test.

That copper and brass were susceptible to the action of the organic acids left in imperfectly refined oils or formed by oxidation of hydrocarbons was well known, as was the consequent fact that the copper cooling coils of air compressors were liable to damage from this cause. But in practice it was unusual to find machinery seriously damaged owing to this action of naphthenic acids on copper and brass. Steel corrosion was a totally different matter. Generally speaking, its mechanical consequences were more immediate and far-reaching, and he would emphasize the point that steel corrosion was practically never attributable to uncontaminated oil. The author had mentioned that no new unused oil had corroded steel under his test, and that his numerous illustrations all referred to used, and therefore more or less contaminated oils. Yet several members seemed to have gained an impression that the lubricating oil refiners were directly to blame for some of the truly awful examples shown.

It was important that there should be no misapprehension on a point affecting the confidence of consumers in the oils supplied to them, and he would like to ask the author to what extent, if any, he had found damage to machinery caused by the corrosive properties of oil, as distinct from substances with which it became contaminated in use.

Mr. J. S. Jackson said he desired to associate himself with the remarks made by the previous speaker—namely, that the author had narrowed the issue down too closely by confining himself to the sulphate value test. The figures for such a test given by the author meant very little unless the history of the oil, its length of service, the fuel with which it had been associated, the moisture content and so on were known. It was not specifically stated whether the oils tested were dry. The fact that the corrosion took place on ships rather than in motor cars was very significant, because of the association of moisture and sodium chloride on a ship. It was well known that those two things would cause considerable corrosion. The actual experiments also called for comment. For instance, the temperature was important, because the conditions under which an oil flowed over the metal surface might be such as to produce conditions which were calculated to cause corrosive action. The author presumably had a fairly thin film of oil running over a heated plate at 90° C., which was a

fairly active temperature calculated to induce oxidation. He thought the author might have extended his operations in relation to the determination of acidic bodies which, although not as violent as sulphuric acid, were worthy of consideration. He desired to associate himself with the remarks made by Dr. Ormandy at the commencement of the discussion to the effect that he had noticed no backwardness on the part of consumers in telling producers what they thought of their products. He had found that the most abnormal ability existed in some chemists to determine acids which were never present. In determining the acidity of an oil the result obtained naturally depended largely on the method of dealing with the oil and the particular indicator used. It was not necessary to confine oneself to the I.P.T. method which, although excellent in itself, was not the only method available. The whole subject was naturally very interesting, but he thought it was necessary to accumulate a great deal more data before it was possible to interpret the results which had been put forward in the paper.

Mr. C. I. Kelly said that he had intended to attack the technique of the Sulphate Value Test, but as previous speakers had already done so he would confine his remarks to one feature of it. He desired to call attention to the nature of the solution from which the barium sulphate was precipitated. Taking the quantities mentioned, this solution would contain about 12 per cent. of potassium chloride by weight. The presence of such a large amount of alkali metal salt was one of the first things that any investigator acquainted with barium sulphate determinations would adopt precautions to avoid. The author referred to the accuracy of the test as being satisfactory. He seriously doubted the accuracy of the test in its present form. Mr. Jackson and Dr. Ormandy had referred to the question of oxidation, particularly at high temperatures, 90° C. He had his attention drawn to a recent case where a high sulphur content oil was used for coating metal parts to protect them from a humid atmosphere. In a few months the shafting had seriously corroded, a recurrence of which was prevented by using a low sulphur content oil. In that connection he desired to draw the attention of the members to a paper by Zaloziecki,[1] who studied the oxidation of petroleum by air. By blowing cold air through oil, the oxidation was slight, but greatly increased in the presence of caustic soda. (This seemed to be borne out by the author's experiences with the alkali treated oils, and at the same time it should be remembered that the oils A, B and C, and particularly the last two, are high in sulphur content.)

[1] *Z. angew. Chem.*, 1891, 416.

According to Zaloziecki, the acidity shown by methyl orange as opposed to phenolphthalein was due to oxidation of mercaptans and organic sulphides and not to traces of acid used in the refining. Hirsch[2] also points out that oils may oxidize at ordinary temperatures when exposed to sunlight, and especially in the presence of alkalis. At higher temperatures, 90° C., the oxidation would proceed much faster and have more serious consequences.

The following written contributions to the discussion were subsequently received:—

From Mr. G. H. Willock.

It would appear that finished oils are passed as neutral to storage tanks fixed with mechanical stirrers to prevent stratification, not covered or insulated, and having leaky coils or other defective equipment as vehicles for pools of water. Is it not possible on the site of such a storage tank, and the works, to have a plant for the regeneration of earths and clays, when the filter material is exhausted and clogged, and it is necessary to regenerate it by heating in a kiln or rotary furnace until waxy accumulation is volatilized? If dust and oily vapours discharge into air offensive odours may be carried for miles apparently in the form of colloidal particles and oily dust, which, coming in contact with contents of storage tank (as mentioned above), combine—i.e., the sulphur products of combustion being soluble in water have corrosive action on metals when such fully oxidized gases are allowed to cool to about 212° F. in contact with certain metals. Dust is harmful, and lubricating oils should be stored in clean tanks, and the barrelling house should be provided with dust free air filter devices to eliminate foreign matter. What is taken out in some refineries is put back in some form at another point. Care must be taken in sampling each tank and not making one sample do for different grades. Mr. Young's procedure and apparatus is a neat and practical one.

From Mr. F. B. Beringer.

With regard to the actual combustion of sulphur-bearing fuels, coal, oil, pyrites, etc., there are three possible sources of corrosion of metallic parts:—

1. Sulphur vapour can attack metals direct forming the sulphides. This must occur but rarely due to the almost instantaneous combustion of the sulphur. Firebox boiler fittings show no signs of this action after years of use.

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[2] *Chem. Ztg.*, 1895, **19**, 41.

2. SO_3 is known to crystallise cast iron under certain critical conditions, so that cast steel is used in its manufacture. This condition is only in comparatively strong concentrations and may be ignored further.

3. At high temperatures SO_3 cannot exist, so that on ignition SO_2 only will be formed. SO_3 begins to be formed on cooling and, in the absence of catalyst, begins some 700° C. with an optiminum at 425° C. tails off again at lower temperatures. The equilibrium value at atmospheric temperature is about 3 per cent. of the total sulphur as SO_2. Further dry SO_3 seems to be unable to seriously attack metals, and even the acid liquid acid does not do so until sufficiently dilute. Steel acid tanks and steel chimneys are both uncorroded.

The conditions for deposition of corrosive acid in cylinders then must be (1) cool surfaces, leaks past piston rings and excess moisture, which also will be brought through from the exhaust gases, all of which are present under the conditions stated by the author.

It is quite noticeable in factories where a furnace or boiler has stopped, and the rain helped to dilute the now cool gases, steel stacks corrode at once, and even the mortar in brick chimneys swells and corrodes. Exhaust piping on Diesels will sooner or later show signs of the same corrosion.

It would look to be a very difficult problem that the Diesel engine manufacturers will be called upon to solve when using sulphurous fuels.

No known treatment of the fuel will serve, acid cannot be prevented from forming, piston rings from wearing and leaking slightly; neutralising direct has proved ineffective in the author's tests.

The probable solution would be continuous cleaning through filters, etc., of the entire oil, or making the piston lubricant a separate circuit and cleaning that.

From **Mr. Sydney J. Tungay.**

It would appear however that the author's observations regarding the corrosion by oil are chiefly restricted to experience on two motor ships, and the corrosion in this particular instance must have been greatly in excess of that usually experienced under similar conditions.

I view with considerable alarm and apprehension the presence of appreciable quantities of H_2SO_4 in lubricating oil, and most certainly agree with Dr. Ormandy that the consumer of oil has some justifiable complaint, if we are to take it that lubricating oils cannot be guaranteed free from appreciable quantities of sulphuric acid or caustic soda.

However, to return to the physical conditions of working under which this excessive corrosion by oil of steel and white metal has taken place, it must be obvious that the D.O.C. test, as described by the author, is far less drastic than the test under actual working conditions—indeed the corrosion shown on specimens submitted to the D.O.C. test apparatus do not indicate any very deep corrosion or pitting, and the metal in most cases would appear to be simply discoloured.

In the case of the actual corroded pins and journals of main shafts in Diesel engines, the oil has not only to work at a fair temperature, but is maintained in the form of a film between rapidly moving surfaces, at the same time being subject to sea mists and a damp atmosphere containing sodium chloride.

No better conditions for an emulsifier could possibly be established, and as we know, emulsification does take place. This, added to the presence of small quantities of H_2SO_4 and chlorides, combined with the working temperature and the rapidly moving surfaces, is clearly a far more drastic test than the continued contact of oil with a heated metal surface as presented in the D.O.C. apparatus.

Assuming that the oil does contain H_2SO_4, and knowing the drastic conditions under which the oil has to work in bearings of sea-going Diesel engines, one is compelled to look into the question of the metal surfaces themselves to ensure that the white metal and the steel used for such work are of such a quality as will best resist the corrosive action of these chemical combinations.

In most of the test specimens illustrated less corrosion is manifest on the white metal than on the steel surfaces. This would doubtless be expected, since the white bearing metals, usually possessing a lead base, would be more resistant to the action of weak acid in the oil.

White metal for bearings is, however, a subject of considerable variation, and an alloy could readily be adopted to combat any corrosion from the oil.

I should not be too ready to condemn the oil refiner, in view of the fact that this oil, when used on similar engines for land service, and consequently under somewhat different physical conditions, will usually be found to show no corrosion.

The appendix to the author's paper is illuminating, dealing as it does with the examination of used oils from motor ships, therein he clearly indicates in his analysis of residue, an appreciable percentage of chloride present.

From Mr. P. L. Wieport.

The writer has had some considerable experience with used oils drawn from the crank cases of engines fitted to heavy motor

vehicles, and agrees that such oils do not give indication of mineral acidity when tested by the I.P.T. Method, L.O.5.

That a used oil is liable to be corrosive may be readily demonstrated without recourse to a test such as has been devised by the author. Used oils invariably contain small, and sometimes comparatively large, quantities of water. On subjecting the oil to careful distillation at ordinary pressure, the first drops condensed are water possessing a strongly acid reaction. The acid is chiefly sulphuric, though nitric acid may also be detected, and, on occasions, nitrous fumes are evident as the first drops emerge from the end of the condenser. It is plain, without further test, that such oils must be corrosive in use, though corrosion of the type described in the paper has certainly not been met with by the writer. In consideration of the ease with which sulphuric acid is derived from the used oil, it seems likely that metallic sulphates are not the sole cause of the corrosion.

A singular omission from the paper is any reference to the sulphur content of the fuel oil employed. This surely is of more importance than the sulphur content of the unused lubricating oil.

Mr. Horace J. Young, replying to the Chairman's remarks, said that in his opinion the great oil-producing firms, as a general rule, are as capable of taking the wide view as are users. The scientist who talked against either was harming science. It was a position—it was always the position—where users and suppliers and scientists representing both must pull together if progress was to result; suppression of facts did no good to anyone and always did harm finally.

He could not agree with the doctrine that because only half of the total number of cylinders on an engine has worn unduly it, therefore, could not be the fault of the fuel oil. Better to say, it might not be. To make two things precisely alike is difficult; to make them work precisely alike is yet more difficult. To assume that the eight cylinders of an engine—and a marine engine at that—are one and all working similarly is to assume that which, in his opinion and experience, is a fallacy. The precise conditions of combustion and of distribution of fuel and lubricant within those eight cylinders are sixteen variables, while the position of each cylinder in relation to that of the others and the ship itself brought in other variables where wear is concerned. Answering the question whether the Sulphate Values are adventitious to the oil, his reply is that where during use the Sulphate Value has increased it would appear to be adventitious. The "academical" dryness of the samples before testing was not ascertained, but in nearly every case water estimations were made. The new oils

were tested in the condition as received; the "acidified" oils were the new oils with the addition of pure concentrated sulphuric acid or sulphates; the used oils drawn from ships or vehicles were tested in the condition in which they were in use.

To Dr. Ormandy he would point out that nowhere in the paper appeared any implication or suggestion whatsoever that "*oils sold contained in fact large quantities of sulphuric acid.*" Dr. Ormandy and other speakers had supplied that implication, and the reasons for their having done so would appear to be known to themselves alone. It had nothing in common with the contents or objects of this paper. Dr. Ormandy might take the point-of-view that corrosion did not affect the car, lorry and cycle trades, but he (the author), having found oils drawn from such sources to be sometimes corrosive to steel or white metal, could not do otherwise than disagree with Dr. Ormandy.

He desired to thank Engineer-Captain Heppel no less for his valuable contribution to the discussion than for his correct and definite enunciation as to what the paper was about. Engineer-Captain Heppel was familiar with the problems with which those in intimate contact with engineering were wrestling unceasingly. He (the author) had found corrosive oil in marine engines where sea water is present often, also in automobile engines where sea-water is present seldom. The phenomenon of sea water in the lubricant on board ship is not uncommon; we are well aware when it happens, what it does and what is done with the oil containing it. The phenomena of the corrosive effects of oil in boilers, condensers and so on is likewise not uncommon. All these things need to be taken into consideration in their proper perspective and degree when considering this paper.

The wear of cylinders and cylinder-liners—about which few facts are told to the world—was a problem falling directly within the boundaries of the subject of this paper. Here, inexplicable things were happening and up to now little light had been thrown upon the subject. He thought it likely that an unprejudiced research upon the effects of burning different fuels in different ways would result in discovering that, sometimes, corrosive compounds were formed which were corrosive under working conditions. People generally seem to have assumed that because acids at certain temperatures do not attack metals it is impossible for corrosion to take place within a cylinder. The sooner we realised that highly corrosive substances were to be found within these cylinders the better. Engineer-Captain Heppel drew attention to the case of compound oils. This was, in itself, an important subject, particularly where such oils passed from compressors through intercoolers into the cylinders.

In reply to Mr. Lomax, he said that tests were carried out on both fresh and used oils and the paper describes which is used in each test. Mr. Lomax appears to think that the author was unable to wash out the alkali as a refiner might be able to do. That was not the position. The whole of the work was directed towards *what a user could do* and when three "laboratory" washings proved insufficient to wash out alkali the procedure was deemed impracticable. Other of Mr. Lomax's remarks were answered in the reply to Dr. Ormandy.

Dr. Thole's opening remarks are covered by the author's reply to Engineer-Captain Heppel.

Dr. Thole goes on to expound an unusual doctrine. In effect he says if one adds sulphuric acid to oil it forms organic compounds which the Inorganic Acid Test is "not intended to estimate." On these lines it would appear to be Dr. Thole's contention that the test is intended only to estimate the acid *before* it is added to the oil, particularly as he points out that he (the author) ought not to have been surprised at its failure to do so *afterwards*. Having provided reasons why the Inorganic Acid Test cannot be expected to function Dr. Thole, giving no reasons whatsoever, concludes with a condemnation of the Sulphate Value Test. He (the author) has no particular brief for the Sulphate Value Test ; it was invaluable to him in his work ; it was the only test he could find which "did the job," and nobody had indicated a better one.

He thanked Mr. Calderwood for pertinently pointing out the failure of the Inorganic Acid Test to show inorganic acid. Mr. Calderwood's work was done independently and it is interesting to know that he too could not find acid after he had put it in. The Sulphate Value Test had not given trouble in forming emulsions ; it was probably a matter of technique. In deference to several clients, it was impossible for him to go into the question of the sources of contamination further than to say that the trouble is by no means confined to one type, class or size of internal combustion engine. He agreed with Mr. Calderwood that it opened out a new line of thought and of investigation on the question of cylinder wear. Possibly the corrosion of bearings is worse where there is a thin film, but more work is needed before one could express an opinion of value.

Mr. Craven says that the whole of the results are simply explained by "free sulphur," and that it was difficult to see how they could be ascribed to "sulphates." In view of the fact that free sulphuric acid or certain sulphates added to uncorrosive oil caused that oil to become corrosive in a similar manner to those under investigation he (the author) concluded that the original source of the trouble was sulphuric acid or sulphates.

Mr. Craven asks how one calculates a result when a known volume of reagent is added to a test and a known proportion of it tapped off and its contents estimated. The answer is that the calculation is done similarly to that of other analytical operations conducted on similar lines.

In reply to Mr. Bowman, who asks whether immersion tests would not give the same result as the D.O.C. apparatus, the answer is in the negative. Moreover, one operator can work 25 D.O.C. tests simultaneously and can ascertain at any moment the progress of any particular one of them without inconvenience, mess or breakage. The simplicity of the contrivance is its advantage; an advantage which makes possible the investigation of large or small numbers of samples in a definite and practical manner. He could assure Mr. Bowman that the Sulphate Value Test was *not* "a true indication of the oil as a corrosive agent"; the paper did not claim it to be so. The Sulphate Value Test was used because it was the only one which gave results when small quantities of sulphuric acid or of certain sulphates had been added to new unused oil. Hence the same test was applied to used oils in which the presence of similar things was suspected. It worked well on used oils.

Mr. Bowrey said that "most oil workers had been in the habit of practising a direct oil-corrosion test of one form or other, not perhaps so elaborate, etc." He (the author's) reply was that his laboratories had done extensive oil testing for some seventeen years and had collaborated with many other large laboratories and this is the first time he knew that a direct corrosion test was a common event. Moreover, if what Mr. Bowrey said was correct, how was the fact explained that we did not know previously that so many service oils were corrosive to steel or white metal. He thanked Mr. Bowrey for pointing out that the paper had not referred to nor placed the blame upon oil-refining.

Mr. Jackson stated that "that the fact that corrosion took place on ships rather than in motor cars was very significant." He (the author) desired to draw Mr. Jackson's attention to the fact that *his paper indicates the precise opposite*, namely, that oils from ships and oils from motor cars are liable to be corrosive in exactly the same manner.

Mr. Jackson mentions an interesting point, namely, "that he has found that the most abnormal ability existed in some chemists to determine acids which never existed." The author, on the contrary, experienced the greatest difficulty in determining acid which he knew existed, because he added it himself.

Mr. Jackson describes the Inorganic Acid Test as "excellent in

itself." Considering that it does not work it would appear that the qualification "in itself" is as inadequate as the test.

Mr. Kelly attacks the Sulphate Value Test. The only thing to do is to find one better for the same purpose. Whilst it is impossible to avoid alkali when alkali is needed, it *is* possible to dilute a solution before proceeding with a sulphate determination. Many "blank" estimations done either with no oil or with oil having no Sulphate Value produced no fact other than that the test was satisfactory.

Mr. Willock's description of the cleaning of the tanks preparatory to loading up with oil for the homeward trip gave food for thought to anyone interested in corrosion by oil. These are practical matters involving the human element and are all important factors in industrial problems.

In reply to Mr. Beringer he thought some of his remarks were much to the point; particularly those where he says "no known treatment of the fuel will serve, acid cannot be prevented from forming, piston rings from wearing and leaking slightly." It is true to say also that neutralising direct has proved ineffective but, on the other hand, another and simpler method has been found whereby the effects are neutralised. Corrosion always proceeds more rapidly when gases have chance to condense or when there is time given for corrosive attack to "get a hold." Probably, in the case of the internal combustion engine, the trouble starts at these periods and, once started, proceeds concurrently hand and glove with wear.

To Mr. Tungay he would point out that the paper made no reference to new oils being contaminated with either sulphuric acid or caustic. It distinctly says that the author had found as yet no new oils which corroded steel or white metal. He (the author) thinks that Mr. Tungay will not suggest that steel which is both pitted and etched or white metal which is nearly entirely eaten away—both of which are visible in many of the photographs—can be said to be discoloured only. Discoloration commonly goes with corrosion; a microscopist might say that it was corrosion. The white metals and steels used were the best Diesel qualities. No lead occurs as a general rule in main bearing white metal used on modern Diesel engines. The white metals in the tests given in this paper contained no other metals than tin, antimony and copper. An experimenter, working upon any particular type of engine, will be wise to conduct his D.O.C. tests with such steels and such white metals as those occurring upon that engine.

Mr. Tungay refers to the presence of chloride in the oils from motor ships. He (the author) has never examined a used marine

oil which did not contain chloride; it is almost a *sine qua non* in merchant ship work. As stated, sea water attacks steel in the D.O.C. test but does so in a different manner to those things which the author has classed under "sulphates." This means no more than that they may be estimated as sulphates by the Sulphate Value Test and that, whatever they are, they give similar effects to those produced when sulphuric acid or certain sulphates are added deliberately to new uncorrosive oil.

It is valuable to note that Mr. Wieport agrees that used oils drawn from heavy motor vehicles do not give indication of acidity when tested by the L.O.5 method. The author cannot agree that careful distillation is as simple as or as good as the D.O.C. Test for ascertaining corrosive qualities; for instance, distillation might not show corrosive sulphates when present in the oil.

The author agrees with Mr. Wieport that the sulphur-content of the fuel employed is more important probably than that of the unused lubricating oil. The paper, however, deals with neither.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

THE ONE HUNDRED AND FOURTH GENERAL MEETING of the Institution of Petroleum Technologists was held at the Royal Society of Arts on Tuesday, November 8th, 1927, Mr. Alfred C. Adams, President, in the chair.

The President said he wished to refer, before proceeding to the regular business of the meeting, to certain announcements which had appeared in trade papers in connection with the reporting of papers which were presented at the general meetings of the Institution. Exception had been taken by certain papers to the present position, and he could not help thinking that some misunderstanding had arisen. The Council authorised him to say that it was far from their intention to adopt any attitude which might be construed as seeking to tie the hands of the press in the reports of the various papers which they published. It was regrettable that an undesirable impression of that kind should arise, and therefore the Council would take such steps as might be necessary to deal with the question as quickly as possible. He made that announcement in view of what had happened in two trade papers on the question with a view to telling the members that the Council intended to remove the misunderstanding as quickly as possible.

The Secretary read the list of members who had been elected since the last meeting, as follows :—

Member.—John Primrose.

Associate Members.—Henry De Wilde, Morris Levine, Wilfred Smallwood, David Mason Walsh, Basil B. Zavoico.

Transfer to Associate Member.—Cyril Spenceley Cleverly.

The President said the members would have the pleasure that evening of listening to a paper on the composition of cracked distillates presented by Professor J. S. S. Brame and Mr. T. G. Hunter. He was sure they would find the subject covered very thoroughly.

Composition of Cracked Distillates.

By Prof. J. S. S. Brame, F.I.C., F.C.S. (Member), and T. G. Hunter, A.R.T.C., A.I.C.

Although the physical and engineering side of the cracking process has developed rapidly within the last few years, the chemical nature of the product has been but partially investigated. Attention has been drawn to this in the Annual Report of the Progress of Naphthology for 1924, in the following comments.

"Very little is known about the chemical composition of the initial charging stocks which are used in cracking, and about as much is known of the final products, while the intermediate reactions are only guessed at."

The classical researches of Thorpe and Young (*Proc. Roy. Soc.*, 1873, 184), have shown that the pyrolytic decomposition of paraffins under pressure is essentially a simple symmetrical splitting of the chain into a lower paraffin and the corresponding olefine. On the other hand, however, the behaviour of naphthenes on pyrolysis is quite unknown.

Engler and his collaborators have demonstrated that the majority of cracked distillates contain all the four general classes of hydrocarbons, unsaturateds, aromatics, naphthenes, and paraffins. The difficulty of ascertaining the composition of such highly complex mixtures arises largely through the lack of satisfactory methods for the isolation of these different classes of hydrocarbons, and the separation of individual compounds. Even the estimation of unsaturated hydrocarbons, in bulk, and the aromatic hydrocarbons in conjunction with the unsaturateds is still in an unsatisfactory state. (J. S. S. Brame, *Journ. Inst. Petr. Techn.*, 1926, **12**, No. 54.)

The present research was undertaken primarily with the object of investigating possible methods of dealing with this problem and applying them, even in an admittedly incompletely developed stage, to the examination of a cracked spirit.

Cracked spirit is sharply distinguished from straight run petrol in its high content of unsaturated hydrocarbons. Since recent work has indicated its freedom from the tendency to detonate in the engine, it now commands a higher price than ordinary petrol. The only disadvantage attendant on its use is the formation of sticky yellow gums, which separate in storage, and are partly dissolved in the spirit and colour it yellow, and are liable to cause

trouble in the engine. This property of gumming is usually ascribed to chemical changes, chiefly oxidation, in the di-olefines, but up to the present hydrocarbons of this type have not been separated from cracked spirit, although Armstrong and Miller (*Trans. Chem. Soc.*, 1888, 74) isolated a derivative of butadiene in the liquid condensate from Pintsch oil gas.

Part I. of this paper is devoted to the investigation of the methods of separating unsaturated and aromatic hydrocarbons from the saturated paraffins and naphthenes, and the much more difficult problem of finding some method applicable to the separation of these two latter classes. Whilst this problem has not been solved completely, a method of obtaining a reasonably high degree of separation has been developed, and it was felt that the methods were sufficiently perfected to warrant their application to a commercial cracked spirit obtained from Russian kerosine in a Cross cracking plant. This forms Part. II. of the present communication.

Part I.

The separation of the component classes of hydrocarbons.—The unsaturated and aromatic hydrocarbons.

The first line of attack on the problem of separation or, in a lesser degree, the concentration of well-defined types of hydrocarbons was that of selective solution in certain solvents. This was suggested from the differences noted in the hydrocarbons rejected and those retained by aniline in the well-known "aniline point" test, especially when several repetitions of the operation were made on the rejected spirit. This preliminary work with the lower boiling fractions of motor spirits was under investigation in conjunction with Mr. L. Samuel prior to the publication of papers by Carpenter and others detailed on page 796.

In many organic solvents the unsaturated and aromatic hydrocarbons exhibit marked differences in solubility from hydrocarbons belonging to the saturated classes. Therefore by fractional extraction, somewhat on the lines of fractional crystallisation, at least sufficient separation should be expected to enable further separation of a more complete order to be attempted by distillation.

The following solvents were investigated :—

(1) Methyl alcohol.

(2) Saturated solution of SO_2 in acetone.

(3) Nitrobenzene.

(4) Di-methyl aniline.

(5) Aniline.

Exhaustive fractional extraction with the above solvents was carried out, both on different cracked spirits and their separate fractions. The degree of separation was ascertained, rapidly and accurately, from change in aniline point before and after each extraction. When a decided difference in the aniline point was observed during any extraction, indicating a radical change in the composition of the spirit, it was confirmed by specific gravity and refractive index measurements. The exact nature of the change was then determined by the estimation of the different classes of hydrocarbons present. Unsaturateds were estimated by volume loss to 88 per cent. H_2SO_4 in a Babcock bottle, the aromatics by the method of Tizard and Marshall (*Journ. Soc. Chem. Ind.*, 1921, 20r), and paraffins and naphthenes by that of Ormandy and Craven (*Journ. Inst. Petr. Techn.*, 1924, **10**, 101).

Although distinct differences exist in the solubilities of unsaturated, aromatic, and saturated hydrocarbons in all of the above solvents, no satisfactory degree of separation was attained. Exhaustive extraction at different temperatures, corresponding to the miscibility temperatures of the different hydrocarbon classes with nitrobenzene, di-methyl aniline and aniline were tried without success. When the petrol distillates were replaced with known binary mixtures of pure hydrocarbons, such as aromatic-paraffin, and aromatic-naphthene, again only negative results were obtained.

In Fig. 1 the aniline points are plotted for mixtures of an aromatic hydrocarbon (benzene) with (*a*) a naphthene (cyclohexane) and (*b*) with commercial hexane (known to be a mixture of *n*hexane and methyl cyclopentane.) The curves rapidly straighten on approaching a high concentration of aromatics, so that the aniline point of a 70 per cent. aromatic concentration with paraffins and naphthenes, and a 50 per cent. concentration with a naphthene alone is not far removed from the aniline point of pure aromatics. Therefore successful extraction with aniline cannot give a much higher concentration than this, namely, 70 per cent. Since a concentration greater than 30 per cent. of aromatics in any extract fraction was never attained, it is evident that the different classes and individual hydrocarbons have a mutual solubility far greater than their solubility in aniline or any other solvent, which renders their separation by extraction impossible.

On the other hand, Mabery (*J. Ind. Eng. Chem.*, 1926, **8**, 814) has used alcohol, and Wilson and Allibone (*Journ. Inst. Petr. Techn.*, 1925, **11**, 180) have used SO_2 in acetone for the successful extraction of unsaturated hydrocarbons from lubricating oil, while Carpenter (*Journ. Inst. Petr. Techn.*, 1926, **12**, 518) has been successful with aniline for the separation of aromatics and unsaturateds from

kerosine, indicating that mutual solubility must decrease with rise in boiling point and molecular weight. The latter investigator also notes an increase in the aniline point of saturated hydrocarbons with rise in molecular weight. In Table I., where the aniline points of some pure hydrocarbons are given, it will be seen that neither the unsaturated nor aromatic hydrocarbons show any appreciable increase in aniline point with rise in molecular weight, so that in the case of the heavier distillates, a still greater difference in solubility between the different classes of hydrocarbons exists, tending to make successful extraction with aniline and similar solvents possible.

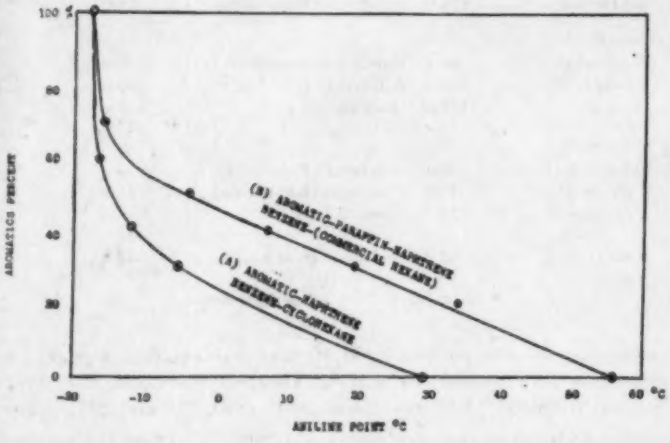

FIG. 1.

Mention might be made here of the great use aniline points have proved throughout the entire investigation, especially in determining the purity of hydrocarbons and as a delicate test for any alteration in the composition of a fraction or distillate. Since practically no data exist as to the aniline points of pure hydrocarbons, these were determined for the very limited number of pure hydrocarbons available, and shown in Table I. Since the aniline point varies with the purity and degree of moisture in the aniline, it is desirable to have some convenient means of standardising this reagent. Heptane from the vegetable source, *Pinus*

TABLE I.

Hydrocarbon.	Boiling point. ° C.	Source of hydrocarbon.	Aniline point. ° C.	C.S.T. in nitro-benzene ° C.
Paraffins—				
Pentane	37·0	Synthetic (Kahlbaum) ..	70·0	23·0
Hexane	68·5	From petroleum (Kahlbaum)	70·0	23·0
Heptane	98·3	Pinus Sabiniana	70·0	23·0
Octane	125·0	Synthetic (Kahlbaum) ..	70·5	23·0
Iso-Paraffins—				
Iso-Pentane ..	28·0	Synthetic (Kahlbaum) ..	77·0	30·2
Iso-Decane* ..	173·0	Synthetic (Kahlbaum) ..	78·0 ..	30·0
Aromatics—				
Benzene	80·4	Pure crystallisable (B.D.H.).	—20·0	—
Xylene	140·0	A.R. (B.D.H.)	—20·0	—
Cumene	152·0	(Kahlbaum)	below —15·0	—
Unsaturateds—				
n-Amylene ..	40·0	Synthetic (Kahlbaum) ..	0·7	—
β Iso-amylene† ..	36·0	Synthetic (Kahlbaum) ..	11·0	—
l. Limonene ..	176·0	Pure (B.D.H.)	below —15·0	—
n-Hexylene ..	62·0	Synthetic (Kahlbaum) ..	16·4	—

* Di-isoamyl. † Trimethylethylene.

Sabiniana, is easily purified by H_2SO_4 and fractionation to 99·99 per cent. pure, comparable to that of Thorpe's specimen, B.P. 98·4 Sp. Gr. 0·70048 $\left(\frac{0}{4}\right)$ (*Trans. Chem. Soc.*, 1880, 216 and 217). The refractive index of our specimen was 1·3892 $\left(N_D^{20}\right)$ (see Discussion).

The aniline used for the above determinations and throughout the investigation was such as to give an A.P. 70·0° C. with a specimen of vegetable heptane corresponding to the given physical constants.

It is seen that the lower normal paraffins have aniline points of 70·0° C., while the iso-paraffins on the other hand have an aniline point 7°—8° C. higher, similar determinations made with nitrobenzene show similar results, a miscibility temperature 7° C. higher. Ormandy and Craven (*Journ. Inst. Petr. Techn.*, 1924, **10**, 101), in their method for the estimation of paraffins and naphthenes by aniline points have assumed an A.P. for all paraffins of 70° C. Since this holds apparently for only the lower normal paraffins, this method is not always applicable to petroleum distillates.

Separation of the unsaturated hydrocarbons by mercuration.—Extraction methods for the isolation of unsaturated and aromatic hydrocarbons having proved unsatisfactory, attention was directed towards chemical methods of separation. Of the two classes being considered here, the unsaturated hydrocarbons are by far the most chemically reactive, therefore if they could be removed and recovered through any of their chemical derivatives, the aromatics remaining can be easily isolated from the saturated hydrocarbons by sulphonation and the subsequent hydrolysis of the sulphonic acids.

Balbiano and Paolini (*Chem. Zeit.*, 1901, **25**, 932, and *Ber.*, 1903, 3574) have employed mercuric acetate for the detection of olefines in light petroleum distillates, the mercuric salt reacting with the olefines at ordinary temperatures. Engler (*American Petroleum Industry*, Vol. II., 521) states that unsaturated hydrocarbons form double compounds with mercuric acetate, and may be recovered by distillation with HCl. Hofmann and Sand (*Ber.*, 1900, 1340) have investigated double compounds of ethylenes

TABLE II.

Mixture employed. Amylene. %	Pentane. %	Amount of mixture used. c.cs.	Amount of mercuric solution. used. c.cs.	Unsaturated hydrocarbons recovered by:	Amylene recovered. % on total used.	Pentane recovered. % on total used.
40	60	20	70	Distilling mercuric compounds of hydrocarbons with HCl.	31	80
33·3	66·6	30	50	Do.	20	100
33·3	66 6	30	50	Decomposing mercuric compounds of hydrocarbons with H_2S and distilling.	15	100

with mercuric acetate, and confirm these reports with respect to ethylene, butylene and propylene. On the other hand, according to the work of Perkin (Brit. Pat., 277) and of Kutscheroff (*Ber.*, 1884, 13), acetylenes give compounds with mercuric salts, the acetate, sulphate and chloride, which are decomposed by mineral acids to form ketones. The reactions of terpenes with mercuric acetate have been studied by Balbiano and Paolini (*Ber.*, 1903, 3574) and by Henderson (*Trans. Chem. Soc.*, 1909, 95 and 289), and in the majority of cases are oxidised by the reagent. However, the possibility of the occurrence of hydrocarbons of either of these two classes, in cracked spirit is extremely remote, and need not therefore be considered here. According to W. Vaubel

(*Ber.*, **21**, R. 185, 717; **24**, 1692) and Kutscheroff (*J. Russ. Chem. Soc.*, **24**, 330) diolefines form precipitates with mercuric chloride, the latter investigator stating that the hydrocarbons may be recovered by distillation with acids. Crossley and Renouf (*Trans. Chem. Soc.*, 1906, 42) and Zelinsky and Lepeschkin (*Ann.*, 1901, 308) report the formation of a precipitate between mercuric chloride and cyclic olefines.

This promising method was investigated first with known mixtures of pentane and amylene, but the recovery of the latter was poor, yet the method may be successfully employed for removal of the olefines leaving unattacked saturated hydrocarbons. It was hoped to improve the recovery of the unsaturateds by the decomposition of the mercury compounds with sulphuretted hydrogen, but this was even less successful than the acid treatment. The results for pentane-amylene mixtures are given in Table II.

Mercuration of the fractions of a cracked spirit, using both the acetate and chloride, did not enable a satisfactory recovery of the unsaturated hydrocarbons to be made, although it did allow of a fairly good removal of them from associated saturated hydrocarbons by refluxing with the acetate.

Although many investigators have suggested the use of mercuric acetate or other mercuric salts for the separation of unsaturated hydrocarbons from petroleum distillates, the reaction has not yet been sufficiently investigated. From our experiments the only conclusion that can be drawn is that mercuric acetate is impracticable for the isolation of unsaturated hydrocarbons from other classes:—

(*a*) Because, only a fraction of the unsaturated hydrocarbons are extracted with the reagent in the cold. Refluxing is necessary to remove the remainder, which are destroyed and lost.

(*b*) Working losses are exceptionally heavy, due to unattacked oil being retained mechanically by the flocculent precipitates formed. It is removed only with difficulty.

(*c*) The reaction is uncertain. Different classes of unsaturated hydrocarbons, and different members of the same class react differently with the reagent. For example, diolefines and the normal olefines give additive compounds, while some isomeric olefines and some of the terpenes and cyclic olefines are oxidised.

(*d*) Lastly, the hydrocarbons, generally, are recovered from their mercury compounds only in a minimal percentage, secondary reactions destroying the remainder.

Separation of the unsaturated hydrocarbons by bromination.—Mercuration having proved impracticable, other derivatives of the unsaturated hydrocarbons were considered.

The additive bromides are readily prepared, and are high boiling liquids or solids, so that the more volatile unattacked hydrocarbons can be removed by distillation. The regeneration of the original hydrocarbon by removal of bromine presents a greater difficulty. The majority of reagents convert the bromides into the corresponding saturated hydrocarbon with elimination of HBr, while the usual practice of heating with sodium is unsatisfactory, since it requires high temperature with large losses through destruction of the bromides.

Armstrong and Miller (*Trans. Chem. Soc.*, 1888, 74), however, in an examination of the liquid condensate from Pintsch oil gas, isolated a bromide of an unsaturated hydrocarbon, from which good yields of the original hydrocarbon were obtained, by the action of the copper-zinc couple.

The reaction was investigated on a pure unsaturated hydrocarbon, the amylene, trimethyl ethylene. A good yield of the bromides was obtained, 91·5 per cent. of the theoretical, and on treatment with the copper-zinc couple in neutral alcoholic solution, a yield of 40 per cent. of the original amylene resulted. The bromination of some of the lower boiling fractions from a cracked spirit was studied, and their bromides isolated by distilling off the unattacked hydrocarbons under reduced pressures. Regeneration of the unsaturated hydrocarbons gave an average yield of 75 per cent. of the total present as estimated to 80 per cent. H_2SO_4, being far in excess of that obtained by the mercuration reaction. The method having proved successful with the lighter fractions, it was applied to heavier distillates, and some exceptionally good yields were recovered, usually in excess of the amount of unsaturated hydrocarbons as estimated by 80 per cent. H_2SO_4. Thus with the 132° C.—138° C. fraction, by 80 per cent. H_2SO_4 the unsaturated content was 8·0 per cent., whilst actually from the bromides 13·7 per cent. of practically pure unsaturated hydrocarbons was recovered with an aniline point of 11·3° C., specific gravity 0·8357 and refractive index 1·4485. This affords a striking confirmation of the conclusions of Moore and Hobson (*Journ. Inst. Petr. Techn.*, 1925, 11, 589), that 80 per cent. H_2SO_4 absorbs only a proportion of the unsaturated hydrocarbons from a mixture with other series of hydrocarbons (aromatics, paraffins and naphthenes).

Separation of paraffins and naphthenes.—Successful separation of the unsaturateds, leaving the aromatics free to be removed by sulphonation, having been accomplished, attention was directed

to the much more difficult separation of paraffins and naphthenes. The residue of paraffins and naphthenes remaining after bromination and sulphonation, in the case of simple mixtures, may be separated more or less into its constituents by repeated fractional distillation. It is, however, very desirable to find some more efficient and expeditious method, particularly as there is always the possibility of the occurrence of constant boiling mixtures.

The work described at the beginning of this paper has shown that extraction methods cannot be successfully applied to light distillates. Previous investigations carried out in conjunction with D. L. Samuel had shown that in a mixture of paraffin and naphthene hydrocarbons, the addition of a third lower or higher boiling liquid, like methyl alcohol or amyl alcohol in a mixture of hexane and cyclohexane, eliminated on distillation a proportion of the lower or higher boiling hydrocarbon preferentially.

This effect was studied on known binary mixtures of paraffin and naphthene hydrocarbons, and it was found that the addition of a third lower or similar boiling liquid greatly increased the separation on distilling. It was found, also, that the addition of a third much higher boiling liquid to a hydrocarbon mixture so altered the vapour pressures, and hence the boiling points of the constituents, that the distillation of the higher boiling hydrocarbon was retarded to a considerable extent. For example, with a given binary mixture, ten fractionations might be required to separate either of the constituents in reasonable quantity and purity. On adding a third higher boiling liquid to the mixture and repeating the fractionations as before, separation could be achieved in four fractionations.

Various attempts at further improvement of this separation were investigated by passing the hydrocarbon vapours, as they issued from the column, through a vessel containing a further quantity of the third liquid, and maintained at a constant temperature. With some mixtures a marked promotion of the separation was noted, but in the majority of cases the improvement, if any, was extremely doubtful. Similar results were obtained by passing a stream of the hot added liquid down the fractionating column itself.

In studying this effect on simple binary mixtures, a mixture of commercial hexane and cyclohexane (50/50) was employed, these being the only two hydrocarbons available in sufficient quantity. To this mixture the third liquid was added, and the whole distilled using a pear bulb dephlegmating column filled with Lessing rings. The vapour temperature, specific gravity and aniline point of every 5 c.c. of distillate were taken.

The composition of the distillates was ascertained from graphs on which the aniline points and specific gravities of different

mixtures of hexane and cyclohexane were plotted. Percentages read from the two graphs were found to agree to within ± 0·5 per cent., correct percentages being assumed to be the mean of the readings from the graphs.

The best liquid for addition to lower boiling hydrocarbon mixtures to improve the distillation was found to be aniline, which has the additional advantage of being easily removed from the distillates by acids. In Table III. the distillation of hexane and cyclohexane with aniline is shown, and for comparison the distillation of the same mixture in the same apparatus without the addition of any third liquid. It will be seen that the composition of the distillate by simple distillation changes but slightly throughout. With the addition of aniline, on the other hand, the distillate gets gradually richer in cyclohexane, until in the last fraction its concentration reaches a maximum of 98 per cent., as compared to a concentration of 64 per cent. in the end fraction without aniline. The general effect of the aniline may be seen in the distillation ranges, that of the mixture alone is 73·5° C.—77·5° C., while the addition of aniline has altered the vapour pressures considerably, tending towards a separation of the constituents, with the whole now distilling between 71·8° C. and 83·0° C.

In Table IV., the distillation from aniline of a sample of hexane as purchased and presumably obtained from a paraffin base spirit, distilling between 68° C. and 71° C., Sp. Gr. 0·6910, and A.P. 56·0° C. is shown. The hexane is being separated into two constituents, one approaching a boiling point of 68° C. and aniline point of 70° C., pure hexane, and another approaching a boiling point of 80° C. and a low aniline point, clearly pointing to the eventual separation of a fairly pure naphthene.

TABLE III.

	Volume of distillate. c.c.	Temp. ° C.	Specific gravity.	Aniline point. ° C.	Composition. Hexane. %	Composition. Cyclohexane. %
Original mixture	—	—	0·7360	40·8	50	50
Distilled alone	10	73·5	0·7210	45·2	66·7	33·3
50 c.c. of mixture	21	74·0	0·7265	44·2	63·0	37·0
	32	75·0	0·7288	42·8	58·0	42·0
	42	76·5	0·7362	40·4	49·0	51·0
	48·5	77·5	0·7470	37·2	36·0	64·0
50 c.c. of mixture	10	71·8	0·7112	49·4	81·0	19·0
Distilled with 50	21	74·0	0·7203	46·7	72·0	28·0
c.c. of aniline in	30	75·0	0·7269	44·4	63·0	37·0
same apparatus	41·5	79·0	0·7453	37·8	39·5	60·5
as above.	48·5	83·0	0·7754	28·3	2·0	98·0

TABLE IV.

	Volume of distillate. c.c.	Temperature. °C.	Aniline point. °C.
100 c.c. commercial hexane (B.D.H.) Sp. gr. 0·6910 A.P. 56·0° C.	10 ..	70·0 ..	62·1
	20 ..	70·0 ..	59·2
	30 ..	71·0 ..	58·9
	43 ..	71·0 ..	58·8
	52 ..	71·0 ..	58·4
Boiling Range { 84%—69–70° C.	63 ..	71·0 ..	59·2
Boiling Range { 98%—71° C.	73 ..	71·0 ..	56·0
	82 ..	73·0 ..	50·6
	90 ..	74·0 ..	48·8
	93 ..	— ..	10·4

TABLE V.

		Percentage of distillate. %	Specific gravity.	Aniline point.	Composition. Hexane. %	Composition. Cyclohexane. %
Original mixture		—	0·736	40·8	50	50
Distilled with methyl alcohol	1st fraction .	20·0	0·7209	45·9	70	30
	Last fraction	9·6	0·7768	27·6	0	100
Distilled with amyl alcohol	1st fraction .	10·0	0·7114	47·6	75	25
	Last fraction	20·0	0·7706	29·6	7	93
Distilled with aniline and methyl alcohol	1st fraction .	30·0	0·7193	46·5	71·5	28·5
	Last fraction	10·6	0·7739	28·8	4	96
Distilled from aniline	1st fraction .	20·0	0·7112	49·4	81·0	19
	Last fraction	14·0	0·7754	28·3	2	98
Original mixture		—	0·7100	49·2	80	20
Distilled with methyl alcohol	1st fraction .	28·0	0·7010	52·3	90	10
	Last fraction	2·0	—	29·5	6	94
Original mixture		—	0·7200	45·5	68	32
Distilled with aniline	1st fraction .	34·0	0·6910	56·0*	100*	0
	Last fraction	4·0	—	27·6	0	100

* For commercial hexane (B.D.H.).

In Table V. the results are given for the distillation of three different hexane-cyclohexane mixtures from four different diluting liquids.

Successful results having been obtained by the use of a third liquid for improving the separation of paraffins and naphthenes by distillation in (*a*) prepared binary mixtures of individual hydrocarbons of each class, and (*b*) a commercial hexane, the method was applied to petroleum distillates already freed from unsaturateds and aromatics. These did not prove so easy of separation as simple binary mixtures. In the majority of cases, however, a fairly good and rapid separation was obtained in a few fractionations. In general, where the fraction was made up of paraffins and a single naphthene hydrocarbon, and the naphthene was the

higher boiling constituent, or when it consisted of some naphthenes and a single higher boiling paraffin, a good separation of the higher boiling constituent was obtained.

The method was utilised quite successfully and enabled a good separation of some iso-paraffins and a fair separation of a number of naphthenes to be made from cracked spirit (see Part II., Table X.).

Part II.

The composition of cracked spirit.—The cracked spirit employed for the investigation was a commercial motor spirit produced by cracking a Russian kerosine in a Cross cracking plant, the sample examined being a distillate direct from the plant, without having undergone any of the usual refining treatment with acids or other reagents.

A clear water white spirit, boiling between 21° C. and 180° C., which, although it showed a gum test (*Inst. Petr. Techn.* method) of 0·055 per cent., did not deposit any gum or become discoloured on standing exposed to the light for over twelve months. On analysis it gave the following figures. Specific gravity 0·751, aniline point 40·0° C., unsaturated content 27·20 per cent. (loss to 85 per cent. H_2SO_4), aromatic content 4·97 per cent. (method of Tizard and Marshall), and saturateds remaining were by difference 67·83 per cent.

In the investigation described here only the lighter portion of the spirit, boiling below 120° C. is dealt with.

Twelve litres of the petrol were fractionated, using a 30 in. column packed with Lessing rings and well lagged with asbestos, into eleven fractions, boiling between 21° C. and 120° C. Using the same apparatus each fraction was again fractionated separately. The cutting points for the fractions in this large scale distillation

Table VI.

Fraction.	Volume of fraction. c.c.	Per cent. on whole spirit. %	Specific gravity.	Refractive index. N_D^{20}	Aniline point. ° C.
21°— 45° C.	585	4·875	0·6497	1·3732	—
45°— 57° C.	420	3·500	0·6680	1·3822	47·0
57°— 68° C.	415	3·458	0·6900	1·3910	45·0
68°— 76° C.	345	2·875	0·7200	1·4017	42·2
76°— 85° C.	370	3·083	0·7260	1·4068	39·0
85°— 94° C.	390	3·250	0·7340	1·4108	41·0
94°— 99° C.	485	4·041	0·7460	1·4164	41·2
99°—104° C.	505	4·208	0·7560	1·4212	38·4
104°—110° C.	410	3·416	0·7540	1·4225	40·0
110°—112° C.	300	2·500	0·7600	1·4230	42·6
112°—120° C.	240	2·000	0·7561	1·4230	44·7

Total distillate, 4465 c.c. Residue, 6577 c.c. Loss, 958 c.c.

were decided upon from the results plotted for a separate distillation of 1500 c.c.

The detailed particulars of the fractionation and the physical properties of each fraction are tabulated in Table VI.

In Table VII. the estimation of the various classes of hydrocarbons present in each fraction are shown.

TABLE VII.

Fraction.	Unsats. %	Aromatics. Benzene. %	Toluene. %	Naphths. %	Paraff. %
21°— 45° C.	36	—	—	—	—
45°— 57° C.	18·0	—	—	28·7	53·3
57°— 68° C.	25·0	3·0	—	15·8	56·2
68°— 76° C.	24·0	2·7	—	25·5	47·8
76°— 85° C.	20·0	2·7	—	33·1	44·2
85°— 94° C.	16·0	3·3	—	42·9	37·8
94°— 99° C.	14·0	4·3*		41·0	40·7
99°—104° C.	20·0	2·1*		54·6	23·3
104°—110° C.	18·0	—	7·5	39·2	35·3
110°—112° C.	6·0	—	12·8	38·8	42·4
112°—120° C.	14·0	—	6·2	32·8	47·0

* As benzene and toluene.

Unsats. By loss to 85% H_2SO_4 in Babcock bottle. (Brame, *Journ. Inst. Petr. Techn.*, 1926, **12**, No. 54.)

Aroms. By aniline point method of Tizard and Marshall. (*J. Soc. Chem. Ind.*, 1921, 20 T.)

Naphs. By aniline point method; see Ormandy and Craven. (*Journ. Inst. Petr. Techn.*, 1924, 101.)

Paraffins. By difference.

As was shown in Part I. (page 798), the determination of naphthenes in admixture with paraffins by the aniline point method is unfortunately of doubtful accuracy, due to the difference in aniline points of paraffins and iso-paraffins, since no alternative method is available it must serve for comparative purposes. It is seen that unsaturated and paraffin hydrocarbons predominate in the lower fractions, but with increasing boiling point the percentage of naphthenes increases up to the fraction 99° C.—104° C., after this the positions are reversed, the amount of naphthenes increasing as the paraffins decrease.

Isolation of the constituent groups.—The first treatment consisted of bromination of each fraction with separation of the unbrominated hydrocarbons by distillation and the recovery of the unsaturated hydrocarbons from their bromides by the action of the copper-zinc, or aluminium-mercury couples (page 801).

The unbrominated portion of each fraction, including aromatic, paraffin and naphthene hydrocarbons, after washing with water,

TABLE VIII.

	Original fraction used.	Isolated unsaturateds.	After removal of unsaturateds.	After removal of unsats. and aroms.
Vol. ..	350 c.c.	60 c.c.	160 c.c.	—
Sp. gr. ..	0·6497	0·6986	0·6566	—
N_D^{20} ..	1·3932	1·3874	1·3761	—
A.P. ..	—	—	—	—
B.P. ..	21°—45° C.	30°—70° C.	25°—73° C.	—
Vol. ..	350 c.c.	66 c.c.	160 c.c.	—
Sp. gr. ..	0·6680	0·7011	0·6660	—
N_D^{20} ..	1·3822	1·3937	1·3795	—
A.P. ..	47·0° C.	—	56·0° C.	—
B.P. ..	45°—57° C.	35°—75° C.	37°—75° C.	—
Vol. ..	400 c.c.	75 c.c.	230 c.c.	185 c.c.
Sp. gr. ..	0·6900	0·7307	0·6860	0·6760
N_D^{20} ..	1·3910	1·4053	1·3850	1·3815
A.P. ..	45·0° C.	—	58·0° C.	61·4° C.
B.P. ..	57°—68° C.	40°—85° C.	45°—85° C.	45°—75° C.
Vol. ..	300 c.c.	50 c.c.	200 c.c.	160 c.c.
Sp. gr. ..	0·7200	0·7177	0·7130	0·6980
N_D^{20} ..	1·4017	1·4079	1·3961	1·3915
A.P. ..	42·2° C.	—	52·7° C.	56·6° C.
B.P. ..	68°—76° C.	60°—95° C.	60°—90° C.	60°—85° C.
Vol. ..	370 c.c.	50 c.c.	240 c.c.	220 c.c.
Sp. gr. ..	0·7260	0·7858	0·7300	0·7200
N_D^{20} ..	1·4068	1·4180	1·4040	1·4004
A.P. ..	39·0° C.	—	50·0° C.	53·1° C.
B.P. ..	76°—85° C.	58°—105° C.	60°—100° C.	60°—100° C.
Vol. ..	370 c.c.	50 c.c.	245 c.c.	220 c.c.
Sp. gr. ..	0·7340	0·7722	0·7360	0·7300
N_D^{20} ..	1·4108	1·4235	1·4085	1·4042
A.P. ..	41·0° C.	—	50·5° C.	54·0° C.
B.P. ..	85°—94° C.	60°—105° C.	85°—100° C.	82°—96° C.
Vol. ..	450 c.c.	58 c.c.	300 c.c.	240 c.c.
Sp. gr. ..	0·7462	—	0·7360	0·7340
N_D^{20} ..	1·4164	1·4265	1·4104	1·4071
A.P. ..	41·2° C.	—	51·0° C.	55·0° C.
B.P. ..	94°—99° C.	65°—120° C.	65°—105° C.	90°—100° C.
Vol. ..	500 c.c.	41 c.c.	382 c.c.	330 c.c.
Sp. gr. ..	0·7560	0·8099	0·7523	0·7457
N_D^{20} ..	1·4212	1·4285	1·4210	1·4138
A.P. ..	38·4° C.	—	47·4° C.	49·9° C.
B.P. ..	99°—104° C.	50°—140° C.	80°—110° C.	97°—110° C.
Vol. ..	380 c.c.	30 c.c.	288 c.c.	240 c.c.
Sp. gr. ..	0·7540	0·8096	0·7581	0·7461
N_D^{20} ..	1·4225	1·4310	—	1·4129
A.P. ..	40·0° C.	—	47·0° C.	54·0° C.
B.P. ..	104°—110° C.	100°—143° C.	80°—120° C.	90°—120° C.
Vol. ..	280 c.c.	6 c.c.	230 c.c.	158 c.c.
Sp. gr. ..	0·7600	—	0·7561	0·7402
N_D^{20} ..	1·4230	1·4324	1·4220	1·4134
A.P. ..	42·6° C.	—	43·7° C.	55·8° C.
B.P. ..	100°—112° C.	100°—150° C.	106°—120° C.	104°—122° C.
Vol. ..	240 c.c.	17 c.c.	165 c.c.	73 c.c.
Sp. gr. ..	0·7561	0·8028	0·7544	0·7542
N_D^{20} ..	1·4230	1·4320	1·4192	1·4201
A.P. ..	44·1° C.	—	50·8° C.	52·3° C.
B.P. ..	112°—120° C.	110°—185° C.	100°—123° C.	110°—125° C.

10 per cent. potash and 85 per cent. H_2SO_4 was redistilled and the physical constants taken.

The aromatics present were removed by sulphonation with four volumes of 98 per cent. H_2SO_4 for some time on a mechanical shaker, followed by additional agitation with two volumes of 98 per cent. H_2SO_4. With this first portion of the spirit, boiling up to 120° C., no attempt was made to recover the aromatics from their sulphonic acids, their estimation as benzene and toluene being considered sufficient.

The saturated portion of the fractions remaining, after washing with distilled water, 10 per cent. KOH, and drying over $CaCl_2$ was redistilled and examined for its physical constants. The details of this process are shown in Table VIII. The unsaturated hydrocarbons have all a higher specific gravity and refractive index than the original fraction and the corresponding saturated hydrocarbons from that fraction. Their aniline points were not determined, but in all cases were very low, being entirely miscible with aniline at ordinary temperatures.

With the lower fractions, the bulk of the isolated hydrocarbon series boiled within the range of the original fraction. With the higher fractions, however, the boiling range of the unsaturated hydrocarbons was almost entirely different from that of the original fractions, while the remaining classes of hydrocarbons, distilled fairly close to the original range. The majority of the fractions appear to be complex constant boiling mixtures.

The saturated constituents.—The remaining portion of the fractions, after the removal of the unsaturated and aromatic hydrocarbons, were each separately fractionated through a 30 in. asbestos lagged column, packed with Lessing rings. The very volatile first fraction, which was entirely paraffin in character, was set aside for separate treatment, and therefore will not be discussed in this communication. With the exception of this first fraction, all the saturated portions were mixtures of paraffins and naphthenes.

After the first fractionation, differential curves showing the amount of distillate collected between each degree centigrade, against the temperature were plotted. After two further fractionations the peaks in the curves had not altered appreciably, and cuts were made at these points which indicate the presence of hydrocarbons boiling about this temperature. The details of the fractions obtained by this method are shown in Table IX.

In Part I., a method for improving the separation of paraffins and naphthenes on fractionation by the addition of aniline, has been described. This method was made use of here for the isolation of some of the paraffin and naphthene hydrocarbons present.

TABLE IX.

Peak cuts.	Sp. gr.	Ref. index N_D^{20}.	Aniline point. ° C.
43°— 48° C.	0·6540	1·3700	69
58°— 64° C.	0·6740	1·3815	63
64°— 71° C.	0·6900	1·3873	58·5
71°— 76° C.	0·7090	1·3956	52·4
76°— 82° C.	0·7250	1·4020	49·0
82°— 87° C.	0·7300	1·4050	50·0
87°— 92° C.	0·7290	1·4047	52·9
92°— 95° C.	0·7290	1·4051	54·5
95°— 97° C.	0·7340	1·4080	53·6
97°—100° C.	0·7400	1·4108	51·0
100°—106° C.	0·7460	1·4148	51·0
106°—110° C.	0·7460	1·4130	55·0
110°—120° C.	0·7460	1·4135	58·0

Naphthenes and iso-paraffins were isolated in varying degrees of purity by fractionation from aniline of the corresponding cut. A mixture of the peak cut with twice its volume of aniline was distilled through a 30 in. lagged column, packed with Lessing rings, and the operation repeated until a good yield of the hydrocarbon in reasonable purity was obtained. No attempt was made to obtain the individual hydrocarbons in a state of absolute purity, it being considered sufficient for the purposes of the present investigation to obtain the single compounds comparatively free from associated hydrocarbons to establish their identity with certainty. However, with only two exceptions, the separated compounds, on comparison of their physical constants with those of the corresponding synthetic hydrocarbon, are of a very high standard of purity.

Methyl hexamethylene was separated from the fraction boiling between 100° C. and 106° C. in a single distillation from aniline. The two side chain pentamethylenes required two fractionations, and hexamethylene was found to be still rather impure after five fractionations. It is remarkable that pentamethylene itself could not be detected in the spirit, so that if it is present at all, it can only be in very minute quantities.

Two fractionations from aniline separated the iso-hexanes, while the iso-heptanes are present in considerable quantity, but for the most part, since their boiling points lie close together, and show a marked tendency to form constant boiling mixtures with each other and associated hydrocarbons, they have up to the present eluded isolation by the aniline fractionation method.

The normal paraffins hexane and heptane are present in association with naphthenes of almost identical boiling range—viz., methyl pentamethylene, and methyl hexamethylene, as constant boiling mixtures. Both the latter hydrocarbons overlap into the next higher fractions, from which they were separated by one or

two distillations from aniline. Where they are associated with the normal paraffins as constant boiling mixtures, it was found that a large number of aniline fractionations would be required to separate the paraffins. Since the volume of these fractions was much too small to permit of this, after increasing the paraffin concentration by several aniline fractionations, the resultant distillate was treated with strong nitric acid to remove the remaining naphthenes. By prolonged and vigorous agitation under a reflux condenser with fuming nitric acid, it was found that, while both the paraffin and naphthene present were attacked, the naphthene was more readily

TABLE X.

Isolated Hydrocarbons.	Physical constants.	Synthetic Physical constants.	Isolated by other investigators. Physical constants.	Investigator.
Trimethyl ethyl methane—				
B.P.	48°—49·7° C.	48°—50° C.	—	—
S.G.	0·6493 (20/4)	0·6490 (20/4)	—	—
N_D^{20}	1·3700	1·3690	—	—
Di-isopropyl—				
B.P.	58°—58·5° C.	58° C.	61·1°—61·2° C.	Brown and Carr, *J.I.E.C.*, 1926, 718.
S.G.	0·6720 (20/4)	0·6700 (17)	0·6600 (20/20)	
N_D^{20}	1·3791	1·3783	—	
n-Hexane—				
B.P.	68° C.	69° C.	68·9°—69° C.	Brown and Carr, *J.I.E.C.*, 1926, 718.
			0·662 (20/20)	
			N_D^{20} 1·3851	
S.G.	0·6729 (20/15)	0·660 (20/4)	68·95	Anderson and Erskine, *J.I.E.C.*, 1924, 263.
N_D^{20}	1·3798	1·3760	0·6767 (15/15)	
			—	
n-Heptane—				
B.P.	98° C.	98·5° C.	98·6°—98·7° C.	Brown and Carr, *J.I.E.C.*, 1926, 7, 718.
S.G.	0·6900 (20/15)	0·6835 (20/20)	0·6893 (20/20)	
N_D^{20}	1·4037	1·3892	1·4068	
Methyl penta-methylene—				
B.P.	73°—74° C.	73° C.	—	—
S.G.	0·7358 (20/4)	0·7430 (20/0)	—	—
N_D^{20}	1·4090	—	—	—
Di-methyl penta-methylene—				
B.P.	93°—94° C.	93° C.	—	—
S.G.	0·7531 (20/4)	0·7530 (20/4)	—	—
N_D^{20}	1·4122	1·4130	—	—
Hexamethylene—				
B.P.	80°—82° C.	80·5° C.	—	—
S.G.	0·7648 (20/4)	0·7780 (20/4)	—	—
N_D^{20}	1·4110	1·4270	—	—
Methyl hexa-methylene—				
B.P.	102° C.	101° C.	—	—
S.G.	0·7696 (20/4)	0·7710 (20/4)	—	—
N_D^{20}	1·4260	1·4270	—	—

acted on. The acid removed the whole of the naphthene with part of the paraffin, to leave a residue of pure paraffin, Hexane and heptane were isolated in this way. Table X. gives particulars of the separated hydrocarbons, while their physical properties are compared with those of the synthetic compounds, and also with the constants obtained by other investigators for identical hydrocarbons isolated from petroleum distillates.

The unsaturated constituents.—The main difficulty in the bromination of unsaturated hydrocarbons present in cracked spirit fractions, especially in the higher ones boiling above 70° C. is the prevention of secondary actions, the bromides having a great tendency to decompose with the formation of thick "tars" and the elimination of HBr. The action of light, heat, the presence of water and probably also oxidation, favour this tar formation (Markownika, *Ann.*, 301, 185, and P. F. Gordon, *J. Soc. Chem. Ind*, 1923, 405 T.). By the use of a suitable diluent the violence of the reaction is lessened, and hence the rise in the temperature of the reaction mixture (Gordon, *J.R.T.C.*, 1925, 53). Unfortunately, the majority of the usual diluents cannot be employed, owing to the great difficulty in removing them from the resultant mixture of oil and bromides. Practically the only possible diluent is glacial acetic acid, which can be removed by water washing. However, it was found that while its use was necessary and quite successful with the fractions up to 60° C., with fractions boiling above 80° C. its presence led to the formation of highly coloured water soluble substances. The production of these coloured products was always followed by heavy tar formation.

With all fractions above 60° C. the use of diluents was dispensed with, the oil cooled to below –20° C., and keeping it well agitated during the addition of bromine. The bromine was added by dropping through a very fine capillary, at the rate of 15–20 c.c. per hour. With the extremely volatile fractions the rate was greatly accelerated, to prevent too much loss by volatilisation, the fraction being well diluted with glacial acetic acid and cooled below –20° C., as before. With perfectly dry oil and bromine, in only a few cases was even a trace of tar obtained.

Despite the comparative instability of the higher bromides to air, light and heat, they are quite readily handled. The washing of the oil and bromides may be conducted normally with distilled water and 10 per cent. KOH. They can be dried over $CaCl_2$, and stored, in the dark, in a tight stoppered bottle which they fill completely, excluding all air.

The separation of the unattacked oil and bromides was accomplished by distillation on a water-bath, under reduced pressure, with the bath temperature not exceeding 70° C. When as much as

possible of the unaltered hydrocarbon had been removed below this temperature, methyl alcohol was added, and the remaining unaltered hydrocarbons distilled over as a constant boiling mixture with the alcohol, below 70° C. as before. This was repeated two or three times until the distillate was no longer a mixture of hydrocarbons and alcohol, but only alcohol. The addition of water separated the hydrocarbons from the alcohol. In this way the bromides were completely freed from unaltered hydrocarbons.

The exact procedure for the recovery of the hydrocarbons from their bromides varied with the different fractions. No attempt was made to further separate the bromides themselves owing to their general instability, it being considered advisable rather to make further attempts at separation into individual constituents on the recovered unsaturated hydrocarbons.

With the fractions boiling up to 60° C., distillation of the bromides in neutral alcoholic solution with pieces of the copper-zinc, or aluminium-mercury couple was sufficient. The regenerated hydrocarbons still contained some unaltered bromides, which were recovered by gently distilling off the unsaturateds, and again treating with the couple. The amount recovered from the bromides was almost quantitative; the only losses incurred being through distillation.

With the distillates above 60° C., this treatment was insufficient, since the bromide mixtures from these distillates contained compounds which are very easily decomposed by heat. It was therefore necessary to distil them initially with the couple under reduced pressure on a water-bath, the bath temperature being kept as low as possible below 70° C. In this way most of the bromides, including those sensitive to heat, are converted into the corresponding hydrocarbons. This distillate, a mixture of alcohol, hydrocarbons, and some unaltered bromides, was added to the residue of unaltered bromides in the flask and the whole redistilled with the couple, at atmospheric pressure. Yields are good but not quantitative, as it is impossible to entirely eliminate decomposition of the bromides during the process.

Refluxing with the couple is not advisable, because some of the unsaturated hydrocarbons are polymerised by the action of the zinc or aluminium salts formed, with high losses. In distilling from the couple, the hydrocarbons are removed from the sphere of reaction almost as soon as they are formed, and loss through polymerisation is practically nil.

These methods were applied successfully to distillates from a cracked spirit boiling up to 140° C.

The unsaturated hydrocarbons isolated from the different fractions, in all 503 c.c. (for details see Table VIII., p. 807), after

being well washed, dried and twice redistilled, were fractionated through an eight-pear bulb column, well lagged with asbestos and packed with Lessing rings. Differential curves of distillate against temperature were plotted, and the hydrocarbons cut into short range fractions where they showed definite peaks.

The possible groups which might be present among these unsaturateds are as follows, olefines, diolefines and cyclic olefines. The formation of dark tars with sulphuric acid, in addition to the polymerised products of the olefines, indicates the presence of diolefines in the fractions boiling up to 60° C., while the high specific gravity of the hydrocarbons boiling above 60° C. points to the presence of cyclic olefines.

Consideration of the literature revealed but slight possibility of isolating all of these component groups, the only alternative which can be considered is the elimination of any two series of hydrocarbons to leave a residue of the third.

The work of Vaubel (*Ber.*, **24**, 1692), Hofmann (*Ber.*, 1906, 3187) and Kutscheroff (*Journ. Russ. Chem. Soc.*, **24**, 330) points to the fact that mercuric chloride reacts with the majority of the diolefines, a compound of the hydrocarbon and mercury salt being precipitated. There is, however, only one case on record where the hydrocarbon was recovered from the precipitated compound (Kutscheroff, *ibid.*). Crossley and Renouf (*Trans. Chem. Soc.*, 1906, 42) and Zelinsky and Lepeschkin (*Ann.*, 1901, 308) report the formation of a precipitate between mercuric chloride and cyclic olefines. The cyclic olefines, and di-olefines, then can possibly be eliminated by the action of this reagent to leave a residue of olefines, although the regeneration of either of the former series is highly improbable.

All the fractions of the isolated unsaturated hydrocarbons were again distilled. This operation could not be carried out until some eight weeks after their first separation, and it was of particular interest to note that the majority showed an increase in specific gravity and refractive index, and also some polymerisation had undoubtedly occurred. In two instances a sharp explosion occurred when distillation was carried practically to dryness. This had never been observed in the re-distillation of the freshly separated hydrocarbons.

Each fraction was agitated with a saturated aqueous solution of mercuric chloride until no further action occurred, and the unattacked portion drawn off and re-distilled. In Table XI., the physical constants of the fractions, before and after treatment with mercuric chloride, are shown, and compared with those of the corresponding olefines.

Such physical constants for olefine hydrocarbons as we have been able to find are included, and in several cases there is fairly

good agreement between some of our olefine fractions and olefines described in the literature. Unfortunately there are many gaps in this literature, and in many cases there are considerable differences in the constants recorded by different observers for what purports to be the same compound.

One troublesome factor has been the variety of temperatures used for both specific gravity and refractive index. This will be evident from Table XI. To make the best comparison possible we actually determined these constants under temperature conditions noted by others.

No claim is therefore put forward that any particular final fraction obtained represents a definite pure olefine, but, nevertheless, taking the boiling range as approximately correct in most instances and the specific gravities and refractive indices into consideration also, it may be claimed that in several fractions the approximation is as close as can be expected to certain well-defined olefines.

Further there is the probability that in some cases, after the mercuric chloride treatment, there is left a mixture of possibly isomeric olefines.

In only one case was any hydrocarbon recovered from the compounds formed with mercuric chloride—namely, from the unsaturated fraction boiling 70°—76° C., and then only in very small quantities. It possessed a distinctly fragrant camphoraceous odour, and was very pale yellow in colour, its physical constants given below, show it to be a cyclic olefine, being in very good agreement with methyl cyclo-pentene :—

Hydrocarbon recovered from mercuric chloride.		Methyl Δ^1 Cyclopentene.
B.P.	66° C.	69° C.
Sp. Gr.	0·769 (20)	0·765 (20)
N_D^{20}	1·4101	1·4130

It is interesting to note here that, during the work with mercuric acetate on the original spirit, described in Part I., the only fraction from which unsaturated hydrocarbons were isolated in any reasonable quantity was that boiling 21°—45° C. Only 5·7 per cent. of the unsaturateds present could be recovered. They possessed the strong and characteristic odour of the fraction, and boiled between 40° and 45° C. Their physical properties are compared below with those of the corresponding fraction 42°—47° C. isolated by bromination, and it will be seen that the two are identical :—

Unsaturateds isolated by bromination.		Unsaturateds isolated by mercuration.
B.P.	42°—47° C.	40°—45° C.
Sp. Gr.	0·6921 (20/15)	0·6912 (20/15)
N_D^{20}	1·3868	1·3860

TABLE XI.

Isolated unsaturated hydrocarbons.	Isolated unsaturated hydrocarbons after mercuric chloride and redistillation.	Physical constants for olefine hydrocarbons of corresponding boiling range.
Vol., c.c. 9 (6) Sp. gr. 0·6763 N_D^{20} 1·3848 B.P. 34°—38° C.	— 0·6820 1·3811 38°—41° C.	1-Pentene (n. Propyl ethylene). — 1·3758 39°—40° C.
Vol., c.c. 3·5 (—) Sp. gr. 0·6835 N_D^{20} 1·3861 B.P. 40°—42° C.	— Too small for treatment. —	3.3-Di-methyl butene (1). 0·6549 1·3766 41·2° C. 2.2-Di-methyl butene (4). — — 40°—42° C.
Vol., c.c. 10 (5) Sp. gr. 0·6936 N_D^{20} 1·3891 B.P. 48°—52° C.	— 0·6846 1·3940 48°—52° C.	No known olefine here.
Vol., c.c. 11·5 (5) Sp. gr. 0·6961 N_D^{20} 1·3936 B.P. 53°—59° C.	— 0·6928 ($^{20}/_4$) 1·3927 52°—62° C.	2.3-Di-methyl pentene (1). 0·680 ($^{20}/_4$) — 56°—59° C.
Vol., c.c. 10 (2) Sp. gr. 0·7133 N_D^{20} 1·3982 B.P. 60°—64° C.	— 0·7178 ($^{15}/_4$) 1·4010 (15) 60°—64° C.	3-Methyl pentene (1). 0·7220 ($^{15}/_4$) 1·3997 (15) 65° C.
Vol., c.c. 30 (10·5) Sp. gr. 0·7140 N_D^{20} 1·4005 B.P. 65°—70° C.	— 0·7031 ($^{20}/_4$) 1·4015 (16) 65°—68° C.	2-Methyl pentene (2) 0·6920 ($^{20}/_4$) 1·4013 (16) 65°—67° C. Isolated hydrocarbon gave a dibromide sp. gr. 1·56 and N_D^{20} 1·5062, while dibromide of 2-me pentene is: Sp. gr. 1·58 to 1·60 and N_D^{20} 1·5062.
Vol., c.c. 20 (9) Sp. gr. 0·7345 N_D^{20} 1·4058 B.P. 70°—76° C.	— 0·7182 ($^{20}/_4$) 1·4044 68°—73° C.	2·3-Di-methyl butene (2). 0·7120 ($^{20}/_4$) 1·4128 72°—74° C.
Vol., c.c. 10·5 (9) Sp. gr. 0·7348 N_D^{20} 1·4107 B.P. 76°—81° C.	— — 1·4100 —	No known olefine here.
Vol., c.c. 13 (3) Sp. gr. 0·7474 N_D^{20} 1·4109 B.P. 82°—89° C.	— 0·7193 ($^{15}/_{15}$) 1·4112 82°—89° C.	5 Methyl hexene (—). 0·7160 ($^{15}/_{15}$) 1·4113 85°—87° C.
Vol., c.c. 13·5 (6) Sp. gr. 0·7428 N_D^{20} 1·4143 B.P. 90°—98° C.	— 0·7305 ($^{25}/_4$) 1·4117 (25) 90° C.	4-Methyl hexene (—). 0·7301 ($^{25}/_4$) 1·4132 (25) 85°—90° C.
Vol., c.c. 14 (9) Sp. gr. 0·7694 N_D^{20} 1·4250 B.P. 98°—105° C.	— 0·7477 1·4200 95°—98° C.	2.3-Di-methyl pentene (2). 0·7355 ($^{0}/_0$) — 92°—95° C. Ethyl pentene (2). 0·7254 ($^{15}/_4$) — 97°—98° C.
Vol., c.c. 10 (1·5) Sp. gr. 0·7702 N_D^{20} 1·4280 B.P. 107°—110° C.	— 0·7574 ($^{25}/_4$) — 105°—112° C.	4-Methyl heptene (4). 0·7411 ($^{15}/_4$) 1·4171 (25) 115° C. 6-Methyl heptene (1). 0·7125 ($^{20}/_4$) 1·3986 111°—112° C.
Vol., c.c. 6·5 (—) Sp. gr. 0·7693 N_D^{20} 1·4274 B.P. 113°—120° C.	— Too small for treatment. —	3-Ethyl hexene (2). 0·7364 ($^{20}/_0$) — 119·4° C. 2-Methyl heptene (2). 0·8160 ($^{20}/_0$) — 123°—125° C.

The figures in brackets after the volumes in the first column represent the volume loss to mercuric chloride.

The diolefine piperylene, b.p. 44°—45° C., if present, should occur in both these above preparations. Both were brominated and from the two individual mixtures of bromides obtained, piperylene tetrabromide, m.p. 115° C., was isolated. This hydrocarbon, which is a butadiene derivative, was the diolefine isolated by Armstrong and Miller (*Trans. Chem. Soc.*, 1888, 194), from the liquid condensate of oil-gas obtained by the decomposition of petroleum at high temperatures. It possesses a characteristic alliaceous odour, which is particularly noticeable in the spirit itself and in the lower fractions after distillation.

Summary.

Whilst no claim is made for the separation of *pure* hydrocarbons of different series from the cracked spirit, although in some cases a close approximation to purity was attained, as judged by the published physical data, sufficiently satisfactory separation and identification appears established for the following hydrocarbons.

Paraffins.—Both paraffins and iso-paraffins are present; hexane, heptane, and the iso-hexanes, trimethyl ethyl methane and di-iso propyl; indications also of the presence of pentane, iso-pentane and iso-heptanes were obtained.

Naphthenes.—These occur with the paraffins, the two being present in nearly equal quantities. Methyl pentamethylene, hexa-methylene, dimethyl pentamethylene and methyl hexa-methylene were isolated, but pentamethylene could not be detected.

Olefines.—These are the predominating unsaturated hydrocarbons in the lower boiling fractions. Those of the type $RCH=CH_2$ appear to be absent, since only one fraction agrees in physical properties of hydrocarbons of this type. Brookes and Humphreys have pointed out that such olefines are unlikely to occur in cracked spirit since they rearrange under the influence of heat—$C_3H_7.CH=CH_2 \rightarrow (CH_3)_2C=CH.CH_3$.

3 and 2-Methyl pentene and 4 and 5-methyl hexene are probable present.

Di-olefines.—Indications of the presence of di-olefines were obtained in the first fractions, with definite evidence of the hydrocarbon piperylene.

Cyclic olefines.—Hydrocarbons of this class predominate among the unsaturateds boiling from 90°—120° C.

Aromatics.—Small percentages of hydrocarbons of this class are present in the spirit. They were assumed to be benzene and

toluene, and determined as such in the individual fractions by the aniline point method before and after sulphonation.

The authors desire to express their thanks to the Power Petroleum Co., Ltd., for the cracked spirit employed in this investigation.

DISCUSSION.

The President said the members had listened to a most interesting paper, and he was quite sure they would be most grateful to the authors for the very earnest and valuable contribution towards a better knowledge of the constitution of cracked spirit and methods of ascertaining its composition. Obviously the paper represented a very great deal of work, particularly when it was considered that it covered and included the examination of the work of other investigators. Although not claiming finality of research in that connection, the paper went a long way towards enlightening their knowledge of procedure in the investigation, and bringing the chemical side more in line with the advance so far made on the physical and engineering side.

Dr. F. B. Thole congratulated the authors on the novel method they had applied to the difficult problem of separating by fractional distillation two hydrocarbons of not dissimilar boiling points. Distillation in the presence of a third component was widely employed for the production of anhydrous alcohol from aqueous alcohol (by the addition of benzole), and the use of aniline as a third component might materially assist the isolation of hydrocarbons from petroleum.

He welcomed the further demonstration of the often proved but insufficiently widely appreciated facts that sulphuric acid was entirely useless as a reagent for the assay of hydrocarbons containing olefines, and that the aniline point was equally unreliable as a means of analysing a mixture of paraffins (normal and branched-chain) with naphthenes.

The development of a method for the analysis of mixtures of hydrocarbons for different types had so far been seriously hampered by the fact that very few definite hydrocarbons are readily available. None of those isolated from petroleum or other natural sources can be relied upon for purity, and many of those on the market labelled "hexane," etc., were manifestly highly impure. A trustworthy analytical method can only be worked out by experiments with mixtures of known composition made up from hydrocarbons which have been prepared by chemical synthesis and which are above suspicion as chemical entities of definite

constitution. Such work must inevitably be laborious but must nevertheless be faced.

Mr. E. C. Craven said the paper dealt more particularly with the question of unsaturateds. He would like to suggest that bromination of a spirit followed by reduction, and obtaining a hydrocarbon in that way did not guarantee that the hydrocarbon was originally present in the spirit. Chemists knew very well that in the bromination of a spirit one always got substitution as well as addition, and it seemed to him that one might very easily prepare a different hydrocarbon from those originally present when one carried out a re-action which was so far-reaching as that of intensive bromination.

He wanted to acknowledge as quickly as possible that the aniline point method for the determination of naphthenes, which the authors had used, was not due to Dr. Ormandy and himself at all. It was due to Tizard and Marshall. He desired to disclaim any credit in connection with it, because in his opinion that method was a particularly bad one. In fact, why it had been adopted on the present occasion he did not know, seeing that Dr. Ormandy and himself had several times published what he thought was a very much sounder method—that was, the determination of the specific refractivity by the Lorentz formula and of the molecular weight. Then by comparing the value so obtained with the formulæ which Dr. Ormandy and himself had published, which were very simple—namely, that the naphthenes were all 0·33, the paraffins were a little bit higher, the unsaturateds higher still, and so on—one could get a very fair knowledge of the composition of a mixture of paraffins and naphthenes. It held very well for bodies of a molecular weight up to 300—precisely where the aniline point method failed.

He had been pleased to see, however, that the authors had used the Tizard and Marshall aniline point method instead of the critical solution temperature method of Chavanne. It sounded very much more imposing scientifically to talk about critical solution temperatures, but in fact the method was purely empirical, so that the simpler Tizard and Marshall aniline point method was to be preferred. Except for binary mixtures of known constituents, however, the aniline methods were only very rough, not only from the divergence which the authors indicated for iso-paraffins, but also because there was no regularity in the aniline point of naphthenes. For example, whilst cyclohexane, methyl cyclohexane and mixed di-methyl cyclohexanes had aniline points of 29, 40 and 61° C. respectively, decahydro-naphthalene of a higher boiling point dropped again to 34° C. So that there

was no possible correlation between the boiling point and the aniline point of naphthalenes; it varied from series to series.

The difficulty of freeing aniline from water was also a nuisance. The aniline point of the heptane used by the authors showed that the aniline contained 0·32 per cent. of water. That amount was sufficient to raise aniline points by 2° C. The true value for heptane with dry aniline was 68° C. It was difficult to believe that even normal paraffins had aniline points of exactly 70° C. apart from the influence of water. The original determinations as quoted by Lomax in the Journal ranged from 69–72° C., and in general the published values for aniline points, and indeed for all other physical properties of pure hydrocarbons, showed wide variations.

If heptane from Pinus Sabiniana were truly normal heptane and not a constant boiling point mixture (of which he was by no means assured), then the value for the refractive index given was far too high. In Dr. Ormandy's laboratory they had prepared many samples distilling entirely within a few hundreds of a degree, and the refractive index had always been within a point or two of 1·3876 $\left(N_D^{20}\right)$ and d20 ·6835.

He would like to ask if the value minus 20° C. for the aniline point of benzene referred to a solid separation. With naphthalene the separation of a solid phase commenced at 50·5° C., but with care one could supercool to 47° without the slightest sign of a true aniline point.

He would like to put on record also that their record books in 1921 showed they were aware of the increase in aniline point with molecular weight for paraffins which was later dealt with by Carpenter. The use of aniline as a preferential solvent had also been tried at that time, and on a 50/50 mixture of heptane-cyclohexane only a 1 per cent. separation had been obtained per operation, so that method had been abandoned as hopeless.

The distillation method with aniline appeared to be a very valuable method of attack in certain cases, but he was not at all sure that that method was likely to show any marked advantage in the long run over straight fractionation. At any rate it was possible to separate the various hydrocarbons mentioned by the authors on pages 8 and 9 in quite as high degree of purity without the use of aniline.

If one applied the specific refractivity method to the values given in Table X. the purity of the various hydrocarbons would be found to vary from about 60 per cent. to nearly pure.

Normal heptane was rather peculiar. He thought it was almost impossible to prepare pure normal heptane from any natural spirit.

The figures given for the specific gravity and the refractive index —and those of Brown and Carr for that matter—were rather extraordinary. The specific refractivity was very much higher than corresponded to any saturated hydrocarbon.

The saturated hydrocarbons from this cracked spirit appeared to be very similar to those obtained from any petroleum spirit whatever. From the Bergius spirit, for example, examined in Dr. Ormandy's laboratory, they had got exactly the same hydrocarbons which the authors mentioned.

The authors had found no pentamethylene. It was extremely difficult to separate by distillation from trimethyl ethyl methane of a similar boiling point. If, however, the appropriate fraction was treated in nitric acid he thought the authors could have separated glutaric acid and have found it was present in that fashion.

Finally, he might be permitted to point out that the main action of sulphuric acid on olefines was not to dissolve them but to convert some two-thirds into heavy paraffins. There was, therefore, no wonder that the authors isolated more olefines than were dissolved by sulphuric. It might interest the chemists present to know that the same reaction obtained with all alcohols containing three or more carbon atoms in the molecule.

Mr. W. J. Wilson felt that it was only by persistent trial of every possible method that the problem could finally be solved. He thought that when the problem was ultimately solved, if it ever was, the end of the difficulties would not have been reached. The next stage would be the interpretation of the analyses made. The authors had referred to differences of properties which were exhibited by unsaturated hydrocarbons of closely similar composition. Was it not to be expected that similar differences would be found in the value of such similar substances in their application as motor fuels? He believed it had been shown that such closely similar hydrocarbons as normal hexane and normal heptane possessed strikingly dissimilar properties when used in the internal combustion engine. Similarly, although chemists had grouped the hydrocarbons known to them in those general characterisations of paraffins, unsaturateds, naphthenes and aromatics, the more one dealt with those substances the more one felt that those classifications were so broad that their meaning was very limited indeed. For example, in a work which had been progressing in his own laboratory in connection with kerosines, it had been found that substances described as naphthenes might be either quite good as burning oils or they might be very bad constituents of an oil, although they were only describable under the present state of

knowledge as naphthenes. Hence it was quite evident from these considerations that when chemists had succeeded in making their analyses of motor fuel or any other mineral oil distillate into those broad classifications, there still remained to them the problem of the interpretation of those analyses.

Dr. A. B. Manning said he would like to add a word or two to the discussion in connection with some work which had recently been done at H.M. Fuel Research Station on the light oils from low-temperature carbonisation. Those, he thought, were somewhat similar in many respects to the cracked spirits which had been described that evening. When he had first started on the problem of their analysis he had come up against many of the difficulties which had been described that evening. The first one had been the question of the treatment with sulphuric acid, and he had early come to the conclusion that no strength of sulphuric acid could give a clean separation between olefines and aromatics, nor possibly either between aromatics and saturated hydrocarbons. A further difficulty in regard to some of the light oils with which he had been dealing had been that he had only a small amount at his disposal, so he had had to devise a modified system of analysis, and finally the following procedure had been followed. He had taken about 0·3 to 0·5 of a gram of the light oil and had vaporised it in a current of air, thence passing the vapour through an absorbing liquid to take out the different constituents. He had found that with pure, or nearly pure, materials with different strengths of sulphuric acid he could not get any clear separation between the different olefines and different aromatics, and he had come to the conclusion that he would have to absorb the aromatics and olefines together. The method he was adopting at the moment was to utilise as absorbing liquid a nitrating mixture, 10 per cent. of nitric acid in sulphuric acid. By that he found he could get a very clear cut between the unsaturateds plus aromatics on the one hand and paraffins plus naphthenes on the other. Under the conditions of the experiment, naphthenes and paraffins were unattacked or at least they were not attacked to more than about $\frac{1}{2}$ per cent. when using a pure paraffin or a pure naphthene. So that that method at any rate he thought gave a very clear separation between the two classes, unsaturated and aromatics on the one hand and saturated and naphthenes on the other. Using a nitrating mixture in that way—(he would not go into details at the moment as he hoped to publish them soon)—he had found it possible to separate the nitro compounds of the aromatics in an almost pure state and weigh them ; and from that he had been able to calculate the original amount of aromatics with only a possible error of a few per cent.,

and by that get the unsaturateds. He thought that the method would develop with further work into a very useful way of examining light oils—oils that could be vaporised readily in a current of air. He suggested the method because there seemed to be considerable difficulties in methods which consisted in shaking oils with sulphuric acid.

The following communication from **Prof. A. W. Nash** was read :

Prof. Brame and Mr. Hunter have described valuable methods for the quantitative separation of the four series of hydrocarbons, namely, aromatics, naphthenes, paraffins and unsaturateds, from cracked spirit.

Unless one has actually been engaged on work of a similar nature, it is extremely difficult to discuss or add anything of value to the findings of these investigators, because under the circumstances such addenda would be more or less conjectural.

Those engaged on research problems connected with petroleum realise how much the work has been handicapped because there has been no reliable means of determining the volumes of unsaturated and aromatic hyrocarbons which an oil fraction may contain.

Messrs. Brame and Hunter have actually obtained an isolation of the unsaturated content of an oil by the action of a zinc-copper couple on the bromides which they give, in neutral alcoholic solution, and have separated the paraffins and naphthenes effectively by fractional distillation in the presence of aniline whereby the higher boiling liquid is retarded. Their support, by experimental evidence, of the conclusions of Moore and Hobson that 80 per cent. sulphuric acid does not effect a complete removal of unsaturateds from hydrocarbon mixtures, confirms what most investigators have realised but have failed to prove.

Whilst this paper, valuable and fundamental as it is, by no means exhausts the subject, nevertheless tribute should be paid to the authors for what would appear to have been a lengthy piece of research, very thoroughly performed, which will prove of extreme value, not only to research workers but the Industry as a whole.

The **President** said there was no doubt that there was a great deal of investigation going on on this very difficult subject, and what he thought the members were indebted to the authors for was that they had come forward and given some direct evidence that work of that kind was going on. No doubt they would have to wait a long time before chemists were in general agreement as to the composition of cracked distillates, but at any rate it seemed to him that they had taken quite a stride forward, and the Institution was very much indebted to the authors for stating the results of their very valuable piece of research work upon which they had

been engaged for some time. He would call upon Prof. Brame to reply to the discussion.

Prof. Brame, in reply, said he must first of all enter a disclaimer. Too much credit had been ascribed to himself and Mr. Hunter by Prof. Nash, in his communication. He had to confess that they had put forward no claim to having developed methods by which the percentage of unsaturateds, paraffins and aromatic hydrocarbons could be quantitatively determined. Having made that disclaimer he would deal with one or two points which had been raised in the discussion. There was their old friend sulphuric acid. They were all agreed that different strengths of sulphuric acid did not do quite what they thought they did do. It was known that 80 per cent. sulphuric acid apparently did not remove everything unsaturated ; in fact, a good deal went into or remained in the spirit. The problem before Mr. Hunter and himself had not been to devise methods for the quantitative analysis of cracked spirit ; they had been really out to separate from cracked spirit as many definite types of hydrocarbons and individual hydrocarbons as could reasonably be done in the course of a not too lengthy research. They had to have some sort of comparison for one fraction of the spirit against another fraction as regards the approximate amount of unsaturated hydrocarbons, etc., and, therefore had to choose some strength of sulphuric acid. They had finally adopted 85 per cent. because it almost corresponded to the definite mono-hydrate of sulphuric acid, and he though it did behave differently to anything outside the hydrate. Recent work of Brooks and Humphreys had shown that to be the case. For the present purpose all that was wanted was some comparison for each of the fractions. The same thing applied with regard to the paraffin and naphthene determinations.

Dr. Thole had mentioned the question of the synthetic hydrocarbons, and had told them about one or two which they could prepare fairly easily. Few had been obtained of a reasonable degree of purity, and as soon as one came to delve into the literature of hydrocarbons it was found that one man's hydrocarbon, say heptane, was not another man's heptane by a long way ; there would be something curious in the refractive index, or other physical property which showed they were not quite the same thing. With organised research, as proposed in the United States, one of the items in the programme was the production of pure hydrocarbons, and the results would give them something better to go on than they had at the present time.

Mr. Craven was not quite sure that they had recovered from brominated products by reduction the hydrocarbons which were

there to start with, because of substitution instead of addition. It was not easy to suppress altogether substitution, but he thought when the bromination was carried out at minus 20 deg. C., and, moreover, that there was present in the material which was being brominated so much which readily and directly combined with bromine, it was unlikely there would be very much bromine which could perform substitution; it would mainly rush into the unsaturated molecule rather than do work in displacing hydrogen from saturated molecules.

The following written communication was subsequently received from the authors :—

It is regretted that when Table I. (aniline points of hydrocarbons) was prepared it was overlooked that Chavanne and Simon had published a table of "Critical Solution Temperatures" in aniline, and in this three iso-paraffins show higher temperatures than the corresponding normal paraffins (*Compt. Rend.*, 1919, **168**. 1111; 1324).

One or two points raised by Mr. Craven and not replied to after the discussion call for brief comment.

Mr. Craven considered the refractive index of heptane, given as 1·3892 $\left(N\frac{20}{D}\right)$ "far too high," and gave the figure 1·3876. In view of this criticism four re-determinations were made with an Abbé refractometer on the same heptane and the mean result was 1·3888 $\left(N\frac{20}{D}\right) \pm 0{\cdot}0002$. We were indebted to Dr. Ormandy for this as a sample of pure (vegetable) heptane.

With reference to Mr. Craven's contention that the hydrocarbons recovered by reduction of the brominated products might not have been present originally in the spirit, owing to substitution probably occurring, the work of Johansen (*J. Ind. & Eng. Chem.*, 1922, **14**, 291) has shown that with the heavier distillates (*e.g.*, a mixture of white medicinal oil with olefines) substitution is negligible at temperatures as high as 25° C., and that it decreases rapidly with fall of temperature. This confirms our view that at −20° C. substitution would be negligible.

Mr. Craven expressed the opinion that the aniline point method for determining paraffins and naphthenes is a particularly bad one, and was astonished at it being adopted. We can agree that results are only approximately correct, but from an article on "A Laboratory Investigation of Motor Fuels" in the *Automobile Engineer* (November, 1927) we gather it has been extensively used in the laboratory with which Mr. Craven is associated, for the author of the above article states that "the accompanying analyses were

in the able hands of Dr. W. R. Ormandy " and the naphthene determinations were made on the formula

$$\text{Naphthenes} = \frac{70^\circ \text{ less A.P. after } H_2SO_4}{0{\cdot}3^\circ \text{ C}}$$

and the paraffins by difference.

With reference to Mr. Craven's emphatic disavowal of the aniline point method for determining naphthenes in the presence of paraffins as being due to Ormandy and Craven, we may have been misled by the following sentence in the paper by these authors on " The Determination of Naphthenes in Petroleum Spirits " (*J. Inst. Petr. Tech.*, 1924, pp. 100-101) :—

" The aniline point of all paraffins being 70° C., the fraction of the washed spirit boiling up to 95° C. contains naphthenes which lower the aniline point at the rate of 0·4° C. per 1 per cent. For the fraction 95 to 120° C., the figure is 0·3° C., and for the residue 0·2° C."

Mr. Craven ascribes the aniline point method we used to Tizard and Marshall, but on reference to the paper by these authors (*i.e.*, the reference quoted in Ormandy and Craven's paper, viz., *J. Soc. Chem. Ind.*, 1921, 20T), the only sentence having any bearing reads : " Chavanne and Simon use the critical solution temperature in aniline to differentiate between naphthenes and paraffins., etc., and to determine the proportions of such hydrocarbons in petrol." Naturally, but apparently erroneously, we ascribed the data quoted above, and which we used, to Ormandy and Craven as being part of their original contribution, and not a reference to Tizard and Marshall's work since they are not to be found in the latter's communication.

THE PRESIDENT said the members had had a very interesting paper and a very interesting discussion. What he always thought about chemists was that it was marvellous how much they differed from one another—sometimes in procedure, sometimes in the results that they obtained, and it was wonderful how they remained such thoroughly good friends. He supposed it was because really they were all working to the same end and with the same aim, and although little points of difference would occur in the end they all came to agree.

In the name of the members he offered a hearty vote of thanks to the authors for the very interesting paper which they had contributed to the Institution's proceedings.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

The NINTH ANNUAL DINNER of the Institution of Petroleum Technologists was held at the Connaught Rooms, Great Queen Street, London, on Tuesday, December 6th, 1927. The Chair was occupied by the President, Mr. Alfred C. Adams, who was supported by Sir Frederick W. Black, K.C.B., and Prof. J. S. S. Brame, Past-Presidents; Mr. Arthur W. Eastlake and Dr. W. R. Ormandy, Vice-Presidents; Mr. Ashley Carter, Mr. A. E. Chambers, Mr. T. Dewhurst, Dr. A. E. Dunstan, Mr. James Kewley, Mr. E. Lawson Lomax, Prof. Alfred W. Nash, Mr. William Sutton, Dr. F. B. Thole and Mr. A. Beeby Thompson, Members of Council; and a large number of members of the Institution.

Among the distinguished guests present were: Lieutenant-General Sir W. Hastings Anderson, G.C.B. (Q.M.G. to the Army), Sir Charles Bedford, LL.D., Sir Robert Waley Cohen, K.B.E., Major H. T. Crozier (H.M. Inspector of Explosives), Dr. W. Cullen, Dr. Frank B. Dehn, Engineer Vice-Admiral Sir R. B. Dixon, K.C.B. (Engineer-in-Chief to the Navy), Mr. Douglas Hacking, O.B.E., M.P. (Secretary, Department of Overseas Trade), Professor J. W. Hinchley, Prof. W. H. Merrett, Mr. G. Patchin (Sir John Cass Technical Institute), Sir Adam B. Ritchie, Prof. Henry Spooner and Sir Duncan Watson.

"The King."

The toast of "The King," proposed by the President, was loyally received.

The President: I have received a telegram from the Rumanian Branch which reads as follows: "Thirty members First Annual Dinner Rumanian Branch, December 2nd, send greetings members London Dinner." I think it is very gratifying to see that our members abroad in the Branches are keeping au fait with what we are doing in London, and have been so kind as to send us this telegram. I am sure you will appreciate it and wish a reply to be sent to them as soon as possible (applause).

"The Petroleum Industry."

Mr. Douglas Hacking, O.B.E., M.P.: What is the association between the petroleum industry and the Department over which I have the honour to preside? What are the interests of the Depart-

ment of Overseas Trade which are also your interests? We are anxious to develop the export trade of this country. We have, as you know, scouts all over the world who are anxious to obtain orders and to interest prospective buyers, and it is our duty to place those prospective buyers in touch with the business world of this country. As I say, we are anxious to develop the export trade. The oil industry mainly depends on the importing of raw material, and the marketing of the refined product. It is true there is some export of the refined products, chiefly to European countries, and that export is, I am told, increasing. It is to be encouraged. At present its proportions are small; the export of refined oil is only just sufficiently great to have attracted me here to-night. If you increase that export, I have no doubt that at the next annual dinner you will be able to approach a Cabinet Minister and get him here instead of me. (Laughter.)

There is an old saying, which must have some truth in it, that the export trade cannot exist without the import trade. If that is so the growth of the import of crude oil into this country is satisfactory. Not only is it satisfactory in itself that we should require such large quantities of crude oil, but it is also satisfactory to know so much of it is turned into valuable products. If we take the year 1921 as our basis, we find that the import of crude petroleum into this country has increased by 600 per cent., while the increase in the import of refined petroleum is only a modest 30 per cent. The present values of our imports are: crude petroleum, £10,000,000; refined petroleum, £35,000,000. I wish, of course, that those two figures could be reversed, but on the whole, they are not unsatisfactory.

We have heard it said that oil is one of the pivotal commodities of commerce. Oil has tremendous uses in this country to-day. The ordinary man in the street looks at motor cars, and expresses in his own mind in terms of motor cars the amount of oil which is being consumed. But the more intelligent members of the community will also take into account that large quantities of oil are consumed in the shipping, engineering and chemical industries, and in the lighting industry. Not only is there the oil which itself is used for lighting, but there is the oil which is turned into electricity. In almost every industrial process in this country lubricants are required, and I suppose a very large percentage of every lubricant is petroleum.

Not long ago I was talking to a man who was very much interested in oil. He came to me with a long face and talked about the wave of over-production in your industry. I do not know—probably nobody here knows for certain—whether or not that over-production is permanent or whether it is only of a temporary nature,

but whichever it may be I am certain the problem will be faced with resolution. There are men at the head of the oil industry who are quite capable of dealing with it. It is impossible for us to be despondent, because when the dividends from the oil concerns are small, at any rate, the price of petrol is low. (Laughter.)

The future of the oil industry is really bright. As I have already inferred, the best consumer of oil is probably the motor industry, and I do not believe (though I am not sure, from the conversation I have had with him to-night, that your President agrees with me) the motor industry has yet reached the saturation point. On this country we have one motor car for every forty of the population, whereas in the U.S.A. there is one for every five. Although we may never reach such a number as five there is no doubt the tendency is in the direction of a larger number of cars, both for pleasure and business, and the more cars that are placed on the roads the greater will be the consumption of the products of the petroleum industry.

Another reason why I think the future of the oil industry is bright is because of the development of the motor ship. A ship driven by motor engines was looked on only a few years ago as a curiosity, but to-day a third of the new tonnage being built in the United Kingdom is motor driven, and I am told that abroad half the tonnage under construction is motor driven. It is interesting to note that the average size of the motor ships under construction to-day is greater than that of the steamships under construction. There are here to-night representatives of the Admiralty and War Office, and were they to speak they could tell you of the vast increase in the use of oil in their two services. There is also a representative of the Air Ministry present, and he could tell us of the enormous amount of oil used by his department.

May I now for a moment turn to the interest taken by the Department of Overseas Trade in your industry. Oil companies are very large purchasers of engineering products. It has been my duty of late to speak on behalf of British goods. I am almost tired of saying that British goods are best, but when you say a thing frequently enough you begin to imagine, at any rate, that it is true. (Laughter.) I wish many of those who are connected with the petroleum industry would repeat to themselves, Coué fashion, that British goods are best. (Hear, hear.) If they did, they might be tempted to place more orders with British engineering firms than they have done in the past. (Hear, hear.) I believe that British goods are the best, and I believe it is worth while paying a higher price for British goods than for those of foreign manufacture. (Hear, hear.) After all, your oil wells may be in very out of the way parts of the world, and if they are you do not want to risk a breakdown, which is very expensive. Thus it is in your interest

to say, perhaps, a little more to make certain you are getting a good article. The iron, steel and engineering trades of this country are to-day in a very depressed condition. Engineering requires help. Some firms in the petroleum industry give more assistance to British engineering than others. I want you to look at the matter to-night, however, not only as a question of patriotism but as a question of good business. Your best customer, at any rate in this country is the business man and the industrialist. If you make his business good by purchasing what he manufactures, you are placing him in a better position to purchase more of your oil. There is no doubt about that. Not only is it a patriotic action for you to place more of your orders with British concerns, but I think it is also a good business proposition. Everyone here must be interested in the general industrial prosperity of the country, and therefore I make no apology for saying a word or two on the subject of our trade in general. There is a subdued optimism in the country at the present time; there is a feeling that better days are not far distant. It is true that some trades to-day are badly hit. It is also true that others are doing fairly well. We are frequently tempted to look at the export trade to give us a good idea of our progress and prosperity. If we take the peak year of recent years—I am referring now to manufactured goods only—we find that in 1924 the exports of manufactured goods from this country amounted to £620,000,000. In 1925 they dropped to £617,000,000. I pass over 1926, because it would not be a fair comparison owing to our trade troubles. The estimated exports for 1927, based on the first nine months of the year, for which we have reliable returns, come to £560,000,000, as compared with £620,000,000 in 1924. That does not look very hopeful on the face of it, but I do not think it is quite a fair comparison. The values of everything have dropped materially since 1924. I have, therefore, taken the trouble to base the export trade for the years 1925 and 1927 on the values of 1924. Then we get a very different picture. In 1924 the exports came to £620,000,000; in 1925, at the values of 1924, the figure would be £628,000,000, an increase of £8,000,000, and in 1927 it would be £630,000,000, an increase of £2,000,000 over 1925 and £10,000,000 over 1924. (Hear, hear.)

Although that may be a small increase, it is at any rate a step in the right direction, and if we progress as I believe we shall I do not see any reason why we should be pessimistic about the next twelve months. I have no idea why the Prime Minister asked me to take my present position, but I do know it was not because I am a pessimist. I am sure you will agree that no pessimist should ever rule over any trade department or over any industrial concern. (Hear, hear.) I believe prosperity will come; it may

come sooner than many of us here imagine. When it does come I believe and hope the petroleum industry will obtain its full share.

I ask you to rise in your places and drink with me the Toast of "The Petroleum Industry." (Applause.)

The Toast was then drunk.

Sir Robert Waley Cohen, K.B.E., who responded, said: I rise to thank Mr. Hacking for the Toast he has proposed and you, Gentlemen, for the way in which you have honoured it. I feel sure I shall be expressing the feeling of all in thanking him for the extremely interesting speech he has just made. (Cheers.)

It seems to me Mr. Hacking bases his hopefulness for the future of our industry to some extent on the great use it will be to the world in time of war. I venture to share his optimism, but rather on the ground of the immense value of our industry in times of peace. It is, of course, an amazingly comprehensive industry. If you reflect what this Toast would have meant when I first entered the industry thirty years ago, it is easy to realise the extraordinary progress we have made. In those days our principal product was kerosine oil, and the petroleum technologists of those days were engaged in helping us to squeeze as much of our product into that fraction as was at all possible. In fact, many of them were engaged in writing letters to the Press denouncing others who had been, perhaps, attempting to squeeze a little too much into that fraction in order to dispose in that way of the then valueless and embarrassing fractions we now call petrol. It was just about that time the motor car came into use. From then onwards, however, all those engaged in the petroleum industry were called upon to create an entirely new industry, which has, of course, far outgrown anything that was thought of at that time. The product which was to be seen burning fiercely at a safe distance from every oilfield became the corner stone of the industry. That is a lesson which I think is typical of the petroleum industry. We never have been and I hope we never shall be in a condition of stable equilibrium. We have always been, we are to-day and I hope we always shall be in that nascent state in which the elements respond most readily to the ingenious activities of the petroleum technologist, and in which, if I have rightly learned the lesson offered to us by the pundits of the chemical world, they are most ready to enter into new combinations. (Laughter.)

Side by side with the creation of that industry, the petroleum business has been called on to create a whole series of new industries in the thirty years which have elapsed since then. I have seen one industry after another grow up and develop into enormous dimensions through the activities of petroleum technologists working,

as I think they always do in our industry, in close co-operation with the industrialists, of whom I may perhaps humbly call myself one. There has been, for instance, the paraffin industry, which has caused the farthing dip of our youth to give way to the beautiful paraffin wax candle of to-day. There has been the bitumen industry, as a result of which the old supremacy of the road as a means of inland transport has been re-established. There has been the mineral lubricating oil industry, which has grown to immense dimensions and is supplanting the vegetable oils of an earlier age, which are now set free for food, and there is the fuel oil industry, which now commands the allegiance of every navy in the world and which —thanks to the invention of the Diesel engine—bids fair to command that of the mercantile marine also.

In fact, a revolution in human activity has been brought about by the creation of this succession of new industries which we call the petroleum industry. It has been a vital factor in the history of the human race, and I think it has been very fortunate indeed in many of the circumstances by which it has been surrounded. Notwithstanding certain occasional evidences of the difficulty which politicians find in resisting the temptation to bring our industry within the embroglio of politics, national or international, we and the other nations of the world have, I think, on the whole escaped this disaster. I think it would be an ill day for the life of any nation if it became anchored to any industry in such a way that the progress and constant movement to which our industry is accustomed became stifled by the bureaucratic regime which is inseparable from any government industry. There are only one or two of the most backward countries in the world which have fallen to that temptation, and my belief is that they will soon come into line with the progressive nations.

Apart from that, the result of our freedom has been that the oil industry has been able to develop almost without artificial shackles of any kind, and competition has taken the form not of useless and wasteful price-cutting but of an honourable emulation in rendering new services to the human race in every country in the world, asking no favour from any people or government, but asking only for an open-minded readiness to give us full credit for the services we are prepared to perform. The petroleum industry, as a result of this, has been, I think, a great force in the constructive progress of the world, and it has been able to build up that position because it rests on a sound, strong, and, if I may say so, above all a profitable basis. We receive from the consumer for our products a price which represents to him the value of those products, in the sense that by paying that price he gets something more valuable than he could get in any other way, something which will give him

the energy he requires more readily and more cheaply and more efficiently than anything else. At the same time we have been able to offer to the great public on whose enterprise, in the long run, the petroleum industry has always depended a sufficient remuneration to encourage and justify them in constantly pouring into this industry a stream of fertilising capital.

Another thing which I think will strike everyone about our industry is that it has always been practically free from the struggles between so-called capital and labour. So far as I know, in our industry there is practically none of those huge armies of capital on the one side and labour on the other, armed to the teeth and ready to engage in gladiatorial conflicts with one another; but in spite of that wages and salaries and the remuneration of the investor are in the oil industry at least as high as in any other industry in the world. I doubt, for instance, whether there is any other industry where the skilled mechanic can command a salary of £1,000 a year, as the driller can in our industry. I think it would take a great deal of gladiatorial combat elsewhere to reach a figure of that sort, which has been attained by us without any trouble at all by the purely economic processes with which the petroleum industry is, I think, uniquely familiar. I attribute this above all to the fact that from its earliest infancy our industry has been conducted by a very close co-operation between scientific men and industrialists. We represent and are reponsible, not to any privileged class, but to great bodies of men and women who have invested their savings, small and large, not in fixed interest bearing loans, but in constructive enterprises capable of carrying the world further forward and upward, and of creating human prosperity. At this moment in the world's history, when we have passed through only comparatively recently a period of unparalleled destruction, I think it would be difficult to imagine any higher purpose a man could set before him on entering on his career than that he should turn his back on the sheltered, regulated industries and activities and throw himself into the front line of that great army which is carrying forward the constructive evolution of the world. If he comes with that spirit into our industry he will help us to open wide the sluice valves of wealth from the hidden resources which lie dormant in the world and which I think as they come out will make the world a much easier and a much more pleasant place to live in than it is to-day. That seems to me a far more constructive task than sitting in the councils of those who merely divide the spoils, and I hope this great society, with its immense numbers of men connected with our industry who are prospering in every corner of the globe, may help us in constantly attracting the best brains in every country to help forward this great industry. (Cheers.)

I said a little earlier that I thought we derived immense benefit from not being tied to any anchorage, and that our prosperity seemed to me due to our being so free from all outside interference with the guiding forces of progress and efficiency. Sometimes governments which look at our great developments and see the wealth which we have created, and are creating, are tempted to ask whether they should not try to conserve it. That is really the opposite process to killing the goose that lays the golden eggs; it is putting the goose into a cage so that its movements are restricted and its productivity decreased. Those who are tempted to do that forget, I think, the chief lesson of the petroleum industry. If so-called conservation were to be imposed on us, so that this generation was deprived of the advantages of free development under which our industry has prospered, can anyone here, with all the great technical talent available in this Institution, guarantee that the next generation will derive the benefit of the artificial restrictions so imposed? Can anyone say the next generation will be dependent on the same sources of energy? We know, for example, that there exist in the very properties of the matter by which we are surrounded sources of energy far more potent than anything which can be got out of oil. These sources are already well known, and it is not a great step forward for the world to discover how they are to be tapped. The day that secret is revealed the oil business will have to be doing something very different from producing oil by the means to which we are accustomed to-day, or indeed by any means of which we can conceive, and the governments which in their wisdom have exercised measures of artificial restriction in order to conserve what appears for the moment to be the most valuable source of energy will find they have missed their market in a very serious way, and that the sacrifices they have imposed on this generation will have served no useful purpose. If we are left alone we shall not allow evolution to overtake us. We shall always, I hope, in the future, as we have been in the past, be ready to create a new series of industries ready to meet the new circumstances as they come along. We are already applying the science of chemistry in a far more scientific and far-reaching way to the products of the oil industry than we have ever done before, and I do not think anyone here would be surprised if at some future meeting to celebrate the prosperity of the petroleum industry it would be the prosperity of producing products not necessarily that they might be burned, but that they might perhaps serve a very much more complex and higher use in the scale of human service.

I will only say in conclusion what I am sure must be clear from what I have already said, namely, that the petroleum industry

is as sound and as strong as it has ever been, and that its health, which you have drunk so kindly and which I think is of such immense importance at this moment for the progress of the world, was never better than it is to-day. Long may it prosper. (Applause.)

"Our Guests."

Sir Frederick W. Black, K.C.B., who proposed the Toast, "Our Guests," said: Mr. Hacking has mentioned white oil; I see here to-night my friend Mr. J. T. Smith, of *Oil News*, who set me a problem the other day by asking me to translate a piece of mediæval Latin. I found it was written in the year 1000 A.D., or thereabouts, by a physician of the Emir of Bokhara, and he prescribed for that gentleman white oil internally. (Laughter.) Furthermore, I have realised that our great ancestor Adam must have known of the uses of petroleum, because his successor and namesake, Sir Adam Ritchie, is finding oil somewhere in the neighbourhood of the Garden of Eden. Not only that, but where he struck oil a great predecessor of his, Alexander the Great, also saw evidence of oil 2,257 years ago, so that oil is at any rate of very respectable antiquity.

Now I must come to my Toast. In this Institution, as you know, we use the word "technologist" as a sort of mantle that covers various professions, and more especially geologists, chemists and engineers. I am going to make use of that principle to-night to deal with the Toast of "Our Guests" in three divisions. Mr. Ashley Carter has furnished me with a wonderful list of the guests present here to-night. It would be impossible to refer to them in anything like detail, and so I am going to divide them into three great groups. First of all there are the distinguished representatives of the Navy and Army, and I believe the Air Force and the Civil Services are not unrepresented. Then there is the general group of guests, including our scientific friends, about whom I shall have a word to say later, and, thirdly, there is the Press.

The Press are commonly spoken of in parliamentary circles as belonging to the Fourth Estate; they are put somewhere down below the House of Lords and the House of Commons. I have lifted them up to-night into the third position. Both in America and in this country I have always had the most friendly relations with the gentlemen of the Press, and I am very glad to-night to be permitted to include them in this Toast.

Now I will pass to our friend, Admiral Sir Robert Dixon, as representing the Navy. I had a talk just now with General Sir Hastings Anderson, Quartermaster-General of the Army, and I said: "You and your naval colleague are not being allowed to speak

to-night." He replied: "Is not that appropriate? We are, after all, the silent services." I believe that to be as true of the Army and the Air Force as from long experience I know it to be true of the Navy. I suppose there is no one who has such huge responsibilities of an engineering character as Sir Robert Dixon, with the great personnel and vast quantity of machinery under his orders. I am sure both he and the Quartermaster-General find they do not get through many days in the official routine without being reminded there is such a thing as petroleum. In the little talk I had with the Quartermaster-General I said to him: "I wonder how all this reorganisation that is taking place in the War Office affects your duties?" He said: "It materially affects my duties." I asked: "Are you getting away from petroleum?" And he replied: "No, I am associated with it more than ever." When we talk of the "mechanisation" of Army transport, we might as well call it "petrolisation," for that is what it is also. I have just learned from the Quartermaster-General that it is no small problem for him not to know what quantities he wants, or what qualities—he can rely on the industry for that—but to know how to organise in detail all the distribution.

I must now pass very rapidly to my other group, our scientific friends. I have been furnished by the Secretary with a long list of distinguished people who are unable to be with us to-night. It includes Sir Joseph Petavel, the President of the Royal Society, Lord Bearsted, Air Vice-Marshal Sir John Higgins and others. I am not going to inflict upon you this other list—*i.e.*, of visitors who are with us—but I am going to pick out one or two typical men.

The first I should like to mention is my friend Mr. Patchin who is doing such good work at the John Cass Institute in training young men already in the industry to learn something more about petroleum, and especially about fuel, and who is arranging at the present time for other lectures on fuel. Then there is Prof. Spooner, Dr. Frank Dehn, Sir Duncan Watson (whom we shall hear presently), Sir Adam Ritchie, and last but not least Dr. Cullen, who is one of our representative men in mining, etc.

I have tried to find out something about Dr. Cullen, and I find he is like all our mining and metallurgical people; he is a much travelled man. I think travelling teaches us above all to be men of the world and sociable fellows, and that is why our guests in a gathering like this will always find a cordial welcome, because we are always glad to see people who have been about the world and who can tell us something.

Dr. Cullen represents the Institution of Mining and Metallurgy. We have heard a lot about them lately. Some of us have been at the dinner of the Mining Conference, and some of our number

went over to Canada to read papers at the Congress there. Anyhow, Dr. Cullen is also a travelled man and a great scientist. I have known times when things have been a little quiet, but to-night we can congratulate our President on the extraordinarily cheerful atmosphere which prevails. I think it must be due to the fact that, as Mr. Hacking and Sir Robert Waley Cohen have told us, things are not so bad in the petroleum world and trade generally, as one may judge from certain surface indications, though surface indications are sometimes apt to be a little misleading.

I will ask you now to drink the Toast of "Our Guests," using "guests" in the most comprehensive sense of the term, to include the Services, the Press and all our other visitors.

The Toast was then drunk.

Dr. W. Cullen LL.D., who responded, said: I feel it a very great honour, indeed, that I have been asked to respond for the guests to-night, particularly when Sir Frederick Black has gone out of his way to couple the responsibility with that of speaking for the Services, the scientific world and the Press. It so happens that, fortunately for me, I can speak for the Services; I hope I can speak for the scientific world, and I have been a contributor to the Press for a great many years.

I have had one or two pointers from the speeches already given to-night, but before I start on them I should like, on behalf of the guests, to thank the Council of the Institution for their hospitality, and I should like to thank Sir Frederick Black personally for the extremely kind way in which he has spoken of the guests. I feel that I am here under somewhat false pretences, because, although it may not be generally known, I am myself actively connected with the business end of the oil industry, so that I feel I really ought to be in the position of a host and not of a guest.

I am supposed to represent the scientific side of the oil industry to-night, which I do not do in the very slightest, but I should like to tell you a little chemical romance, which I think is probably quite unknown to any single individual in this assembly to-night. I have been all my life connected with the explosives industry As those of you who are engaged in the production of oil know, in certain geological formations nitro-glycerine is frequently used to tickle up wells that have become sluggish. Within the last few years, however, nitro-glycerine, owing to the scarcity of glycerine, has become somewhat expensive. All over the world, as you know, oil is accompanied by the evolution of great quantities of gas. That gas consists very largely of ethane, C_2H_6, and it cracks exactly as petroleum cracks, forming ethylene, which after going through a series of chemical operations becomes glycol.

Glycol is a substitute for glycerine and therefore in its nitrated form a substitute for nitro-glycerine. The little romance is this, that arising out of that by-product of the oil industry we get a product which goes back into the ground again in the form of di-nitro-glycol and is used for the tickling up of these oil wells. (Laughter.)

Some time ago I got, as many of you did, the Minutes of the Congress held recently in Canada, which unfortunately I could not attend, and I noticed there that a resolution was proposed to the effect that certain societies which had cognate interests should make an endeavour to get housed under the same roof. Personally, I feel this is a matter which should not be rushed, but I feel that three societies, your own Institution, the Institution of Mining and Metallurgy and the Institution of Mining Engineers—embodying the four branches of applied science, engineering, chemistry, physics and geology—should be brought into closer contact with one another. It is quite true the chemical fraternity, to which I am supposed to belong, have talked a lot on this subject in the last six or seven years, but nothing has been done. In the mining industry, however, we have already accomplished something. The Institution of Mining and Metallurgy and the Institution of Mining Engineers are co-operating together, and have done so for a number of years, in the most friendly and efficient way. I think you have only to carry things one step further and get all three under one umbrella. There is no use disguising the fact that money will be required, but I think the rumour can be substantiated that there are certain people in the oil industry who have, or may have, a little money to spare for the foundation of such an institution as I have in mind. I merely throw out this hint to them, and if necessary I shall repeat it everywhere I go. At any rate, I think the first step is to get these three bodies to combine and work together in closer co-operation.

There is another point arising out of much the same considerations. I think this and the other societies with which I am connected have devoted themselves too much in the past, probably, to the purely technical aspects of the industries with which they are connected. That is only one chapter in the story, as you all know perfectly well; there is the other side—the business and economic side. I do think the three technical societies I have mentioned are incomplete unless they have some form of membership which will admit business men, who know the economics and the costings side of the particular industry with which they are connected, because, as I have mentioned already, the technical side is, as a general rule, only chapter one and possibly the least important chapter of all.

I am afraid I have trespassed on your time long enough, but I should like for a moment to go outside the sphere of petroleum production and devote a word or two to some sidelines of it before I sit down. In the course of my business I have to keep in touch with questions of low and high temperature carbonisation, shale distillation and the synthetic production of oil. I suppose, speaking broadly, that if we were to exploit high temperature and low temperature carbonisation to their utmost limits in this country—or in any country—it would make practically no difference to the oil position as we know it to-day. With regard to shale, as far as I can judge, with the present price of oil, I think we may look on shale as a reserve which the Almighty has placed in the ground against the time when oil will really be scarce—of which we see no chance just now at all. One is apt to be a little alarmed after reading articles in the Press about the synthetic production of oil, either by the Bergius process—Berginisation—or by the other process which synthesises the gases of coal right up to the production of oil. As far as I have been able to judge—and I speak with more knowledge of these processes, probably, than the ordinary man in the street—I think we shall have to wait a good many years before the technical difficulties, which are very evident, can be overcome. Moreover, if one commences to think of the capital outlay required for the production of one million tons of oil the figures are staggering.

I thank you very much for the patience with which you have listened to these remarks of mine, and I thank you again for the way in which you have received this Toast and Sir Frederick Black for the way in which he proposed it. (Applause.)

"The Institution of Petroleum Technologists and the President."

Sir Duncan Watson, who proposed the Toast, said: I have the honour to propose a Toast which I am sure will be received by every one here present with acclamation; it is the Toast of "The Institution of Petroleum Technologists and the President." You will receive this Toast with acclamation, not on account of anything I may say, but because you anticipate that in his reply the President will be able to tell you of the development and progress of your Institution. I remember the time when I knew practically nothing of your Institution. I cannot help thinking that if I had done nothing more than listen to the excellent speeches which we have heard and appreciated this evening I should be in a position, without having had access to your Journals, to say something as to your importance and your position.

All of us in the engineering world—with which I am happily or unhappily associated—realise that yours is a wonderful and a

growing industry. You have in your body a section which can but prosper by publicity—I refer to the marketing and transport side. That has its humorous side as well.

Many people feel that the real combat between coal and oil as fuel has only just begun. I personally am perhaps most intimately interested in the question of economic powers of production, and I am interested especially in these days with the threatened competition of fuel in its latest application, namely pulverised fuel. That at once gives you an indication of the vast possibilities you have as petroleum technologists of combating the competition you will have to face very shortly.

Now, gentlemen, we know very well that in these days of intense competition no industry of any importance can afford to be detached from its technology. We have only to refer, as we must, of course, to the amounts which are spent in America and Germany on research. We find there that every industry is associated to-day with its technological experts.

I was very interested in the remarks of Dr. Cullen. I remember the time when it was infra dig. for an institution to be associated with the commercial aspects of the industry with which it was connected, but I think those days have passed, and to-day we find in the Institution of Electrical Engineers—a somewhat insular and professional body—that they and others are paying attention to the commercial side of the industry, realising that with the prosperity of the industry they are very largely identified.

I find that your Institution comprises geologists, chemists and engineers, and, I understand, also the transportation and commercial sides of the great industry with which you are bound up. From experience I should say that that was a very difficult team to run in single harness, and I congratulate your President and your Institution on the harmonious and successful understanding which exists between these different sections.

What a wonderful demonstration your industry was able to give during the General Strike! I happened to be in a position of considerable responsibility at the time, and I am perfectly certain that if those responsible for the control of organised labour had realised the vast importance and the adaptability and flexibility of motor transport that strike would never have taken place. I regard your industry to-day as one of the most potent and effective influences for domestic peace; an industry with such influence and potentialities as yours is one of the most effective supports of constitutional government.

This Toast would not be complete if I did not refer to your very distinguished President. (Cheers). I have known your President for over a quarter of a century, and it speaks volumes for his

sagacity, friendship and generosity that we are still friends. To praise him would be like sending coals to Newcastle—or shall I be up to date and say like sending oil to Thames Haven.

I should just like to say this. An Institution constituted as is yours, important and progressive as it must be, is very happily situated in having a man whose great personal and professional and business attainments qualify him for the highest position to which you can elect him. (Cheers). I am perfectly satisfied that when his term of office comes to an end you will agree with me that, however successful his predecessors, there is none who will be more genuinely appreciated and remembered by you than Mr. Alfred C. Adams. (Applause.)

The Toast was enthusiastically received.

The President who was received with loud applause on rising to respond, said: I must first thank Sir Duncan Watson very warmly for proposing the Toast in such generous and complimentary terms, and the members and our guests for receiving it with so much cordiality. I think the Institution is to be congratulated on having the good fortune to obtain a man so well known as Sir Duncan Watson to propose this Toast. We welcome him as a distinguished leader in the field of electricity and electrical supply, which he has done so much to promote. We regard electricity as a great sister source of power—or perhaps Sir Duncan will allow me to call it an emanation of the power supplied by petroleum. ("Hear, hear.") I was glad to hear that Sir Duncan thinks so well of us, because we should like nothing better than to stand well with him. He is engaged in great works in the electrical world, and I am sure we may be of very considerable use to the great power for which he is working so hard.

In looking round this auspicious gathering, remembering that it represents the best brains of the scientific world and that the Institution includes among its members so many diverse professions—geologists, chemists, engineers, drillers, field managers and others—all working on petroleum in their different ways in all parts of the world, I am irresistibly convinced that here we have a tangible example of that priceless commodity known to us Nature's Own Mixture (applause); and when we consider that each one is animated, as he should be, by the spirit of "anti-knock," we seem to have all the proper elements necessary to a driving force suitable for the most exacting needs of the petroleum industry and the services to which it contributes power.

In this year our Institution will have completed its fourteenth year of existence. Its membership has been steadily increasing with each year since its incorporation. I am now able to tell you

—and it affords me very great pleasure to be able to do so—that the elected membership of all classes now amounts to a thousand. (Applause.) To be exact, it will reach and indeed exceed that figure as soon as Council next meets. Beyond that we have still further applications for membership which have not yet passed the ordeal of the ballot. That, I think, shows that the Institution is going ahead. (Applause.) There is something satisfying in a round number like that, and it is, I think, noteworthy because we may regard it as marking our arrival at a point at which our ideas may be allowed to expand and we may permit our minds to roam over wider fields of endeavour than were open to us in our younger days.

Naturally in its earlier days the Institution had to establish and consolidate the position it sought to occupy. It had to justify the foresight and example of its first President, the late Sir Boverton Redwood, who, more than any of those associated with him, was its prime founder. Although of necessity it builded slowly at first, we may congratulate ourselves that to-day the Institution is established on a sound basis, not only in its finances but also in the reputation which I am happy to think it enjoys and deserves throughout the oil world. In speaking thus I do not forget that in its early days the Institution was the recipient of much generous aid from those great oil companies whose help has always been forthcoming in support of a worthy effort for the advancement of science and its aims. To the great value of that help, which we still enjoy, I feel myself particularly qualified to testify. (Applause.)

I personally, as Chairman of the Finance Committee, which position I held until I was elected President, was entrusted with the care of the Institution's finances, and I am glad of the opportunity this gives me to offer to those Companies on behalf of the Institution my word of grateful thanks for having enabled us to do so much that we could not have done without their assistance. (Applause.)

It was through the kindly interest of the late Lord Cowdray—always a firm friend of the Institution, and one of its founders—that needed impetus was given to our Students' Section, and a little later this became more firmly established through the friendly help of the Anglo-American Oil Company. Our Students' Section now numbers 115 members. Some of these we do not see; they are occupied with duties in many parts of the world; but regular monthly meetings are held at our headquarters in London and at Birmingham by those who are at home, and all that is possible is done to help them in their studies.

It has been said that this Institution in some respects controls the destinies of the oil industry because of the influence exercised

by its members in the scientific development of oil winning and working. On an occasion such as this it is common to indulge in frivolous allusion to "Wine that maketh glad the heart of man," with its inevitable continuation by further allusion to "Oil that maketh him of a cheerful countenance." (Laughter.) That is all very well, but if we applaud the wisdom of the great man who gave utterance to this comforting thought, we technologists, in remembering our responsibilities, must not forget that reputedly an even wiser man than the psalmist administered the warning that "He that loveth wine and oil shall not be rich." (Laughter.) It is not known what circumstances influenced the expression of this somewhat depressing admonition. It may have been due to a natural outburst of disappointment following the unsuccessful result of some venture in digging for oil which did not yield the hoped-for gusher and so convert the Ships of Tarshish into tankers. (Laughter.)

Sir Duncan Watson has referred in terms of praise to our Journal. We shall have issued this year six numbers of our Journal, and it is now much enlarged and includes, in addition to the papers read at our monthly meetings together with the discussions thereon, many reviews and abstracts of a great mass of work in connection with petroleum technology. Our thanks are due to our Honorary Editor, Dr. A. E. Dunstan, whose untiring and successful efforts have maintained the high standard set in previous years. The increasing demand for the Journal of the Institution is a very good criterion of the esteem in which it is held in the scientific world and there is no doubt that it is widely read and much valuable information is contained in its pages. I hope it may not be very long before the Journal is issued monthly ("Hear, hear"), because I think in that form it would be even more appreciated than it is now.

The work of the Institution during the past year has been of a somewhat varied character. Apart from representation on a number of bodies whose activities are of a more permanent nature, our representatives have taken part in the Seventh Congrès de Chimie Industrielle, held in Paris, which formed a prelude to the celebrations in connection with the centenary of Marcelin Berthelot, at which I had the honour of representing the Institution. Special mention should also be made of the Second Triennial Empire Mining and Metallurgical Congress held in Canada, at which a set of important papers were contributed by Sir Thomas Holland, Sir Frederick Black, Professor Nash, Mr. Cunningham Craig and Mr. McConnell Sanders, forming a complete survey of the problem of petroleum from the Empire point of view. Our thanks are due to Sir Thomas Holland and Professor Nash, who officially represented the Institution at this Congress in Canada.

The Standardization Committee has been very busy on the revision of the "Book of Standard Methods of Testing Petroleum and its Products." It is probable that the revised book will be ready for issue in the first half of next year, and it will be a valuable handbook which will be much sought after. The Standardisation Committee is presided over by Sir Frederick Black, to whom and to whose colleagues we are indebted for much painstaking and laborious work. (Applause.)

We have established two branches, one in Rumania, and one in Persia. The telegram I read earlier in the evening came from Rumania and indicates that that branch is going strong. The advisability of forming other branches is under consideration.

I must thank Sir Duncan Watson for his generous references to myself, though I hardly feel I deserve them. At any rate, I realise I entered on my presidential existence so much in the crude condition. I am trying to retain the good will extended to me when I started, and I am pleased to be able to say that the current year, so far, has been happily filled for me in undergoing a process of gentle saturation at your hands. (Laughter.) I appreciate this the more because it has given me the opportunity of officially improving my acquaintance with such—to me—elusive bodies as the common olefines and of contemplating and mingling with the aromatic aristocracy. It has so far been my fortune to escape being subjected to a process of refining that might result in my spirit becoming cracked, and this is just as well, since, in any case, high temperatures and pressure do not suit my constitution. (Laughter.) If I am lucky I may presently emerge a perfectly refined product, but I entertain some doubts of that. My hope, however, is that when my term of office is done I shall come to be regarded as a catalytic body which, whilst unchanged in itself, has performed its proper function in assisting the combination and association of the elements of technology and commerce, and perhaps has been the means of helping to create new derivatives. (Applause.)

Once more I thank Sir Duncan Watson for the good wishes he has expressed for the welfare of the Institution. We hope to deserve them.

I will now, on your behalf, say a few words in appreciation of our officers, on whom falls a great burden of work that never relaxes. There is our Honorary Secretary, Mr. Arthur W. Eastlake, who keeps unsleeping vigil over all our doings and chides us when we seem to be exhibiting signs of undesirable precocity, or in danger of overstepping the limits allowed by his parental indulgence. We have no more zealous supporter than our Honorary Secretary. (Applause.)

I have alluded to Dr. Dunstan's fine work as Honorary Editor (applause), but our thanks are also due to Mr. G. Sell, who carries out the duty of Assistant Editor with so much success and who is also Secretary of the Standardization Committee. (Applause.)

I must not forget Mr. Ashley Carter, to whom we are indebted for the arrangements made for our comfort at this dinner. (Applause.) A special word of thanks should be reserved for our indefatigable Secretary, Commander R. E. Stokes-Rees, R.N. (Applause.) My predecessors in the chair have said nearly all there is to say about him, but I should like to pay my personal tribute to his untiring efforts in the interests of the Institution. He is assisted by a very efficient staff, to whom also the Institution owes a full measure of thanks.

I have told you as briefly as I can something of what the Institution is doing and the work it has got through in the course of the year. All its members are very busily engaged, and a proper recital of all they do would take far too long, and I will not inflict it upon you. I have only to offer you, therefore, the greetings of the season which is now approaching, and to express the wish that you will all enjoy a happy and prosperous New Year. (Prolonged applause.)

The Action of Strong Sulphuric Acid on Olefines and Alcohols.*

By W. R. Ormandy, D.Sc., F.I.C., F.C.S., M.I.A.E., and E. C. Craven, B.Sc., F.C.S. (Members).

Little work has been published on the action of concentrated sulphuric acid on olefines or alcohols containing three or more carbon atoms. In the case of amylene the action of weaker acid has been investigated, and found to give rise to di-polymers.[1] [2]

Plant and Sidgewick[3] found that acid of 97 per cent. strength at 25° C. absorbed 50 per cent. of propylene in two hours. A colourless oil separated which boiled from 55—155° C. at 30 mm. The fractions appeared to react with sodium and were thought to be mixtures of open chain secondary alcohols. The theory was put forward that propylene polymerises to $CH_3(CH_2)_{3n}CH{:}CH_2$, sulphuric acid is then attached at the double bond and subsequent hydrolysis yields alcohols. The molecular weight of the colourless oil indicated a molecular complexity of about C_{12}.

A very early observation by Berthelot[4] on the same olefine states that di-isopropyl sulphate separates, which is decomposed and dissolved by cold water.

Some recent work by the present authors[5] on mixed amylenes from fusel oil indicated a reaction of a very different type. One volume of the amylenes run slowly into 3 volumes of sulphuric acid of 98 per cent. strength gave about 70 per cent. by weight of a colourless oil which proved on examination to be a mixture of saturated hydrocarbons, probably open-chain paraffins. The acid on dilution and steam distillation gave some highly unsaturated oils which appeared to be triolefines. No alcohols were found in the aqueous distillate.

Further work has shown that this reaction is general with olefines or their parent alcohols containing three or more atoms of carbon. With excess of sulphuric acid paraffins and unsaturated oils are formed. The reaction appeared to proceed through the formation of alkyl sulphates which then further dehydrate at room temperature giving rise to hydrocarbons.

This formation of hydrocarbons is referred to by Wichelhaus, "Sulphurien u.s.w.," 1911, in treating of the action of sulphuric at 100° C. on alcohols: "Weniger gut lassen sich so höhere

* Paper received July 29th, 1927.

Homologe darstellen, da sich diese Alcohole unter Entwicklung von schwefliger Säure und Bildung von Kohlenwasserstoffen zersetzen bei Einwerkung der Konzentrierten Säure."

It is obvious that this formation of paraffins must materially influence any attempt made to determine the proportion of unsaturated hydrocarbons in petroleum spirits or the like by any test involving the use of strong sulphuric acid. The change of aniline point on washing out with acid will also be affected.

In examining the hydrocarbons considerable use has been made of the Lorenz-Lorentz specific refractivity values :—

$$r_L = \frac{n^2-1}{(n^2+2)d}$$

The following values have been used for the molecular refractions :—

C=2·418 H=1,100 Double bond 1·753

giving :—

	r_L
Open-chain paraffins	0·3299+1·54/M
Naphthenes	0·3299
Bicyclic naphthenes	0·3299—1·54/M
Olefines	0·3299+2·39/M

where M=mol. wt.

Experimental.

Olefines.

(1) *Ethylene.*—Ethylene was prepared by the passage of the vapour of pure ethyl alcohol over heated phosphoric acid on pumice. The gas was purified by passing over potash sticks and granular calcium chloride.

On bubbling the gas slowly into 98 per cent. strength sulphuric acid for some hours considerable increase in weight occurred, but there was no separation of oils. On dilution with water a clear solution was obtained which yielded ethyl alcohol on boiling. There was therefore no evidence of the formation of hydrocarbons in this reaction.

(2) *Propylene.*—Propylene was prepared by dropping *n*-propyl bromide into boiling alcoholic potash. The method was found to be unsatisfactory, much propyl alcohol being formed and little propylene. The latter passed into 98 per cent. H_2SO_4 gave a colourless oil n_D 20° C.=1·442.

Propylene was prepared more conveniently by passing the vapour of isopropyl alcohol over phosphoric acid on pumice in a heated silica tube. The gas after cooling was passed over potash sticks and calcium chloride.

The vapour density at N.T.P. was found to be 21·59 (H=1) v.d. C_3H_6=21. Beilstein gives (1·498 air=1)=21·55.[6] It was not certain that the gas did not contain a small amount of volatile polymers particularly since a small amount of light oil separated in the cooling system. The gas was completely absorbed by excess of conc. H_2SO_4 in a gas pipette.

In an initial experiment a brisk stream of propylene was passed into 5 c.c. of 98 per cent. H_2SO_4 in a triple potash bulb cooled by tap-water. It was observed that until a large oil layer had formed in the first bulb no gas passed into the second bulb and this in turn absorbed completely for a very considerable period. The increase in weight of the acid was as follows :—

1 hour	54·1%	4 hours	98·0%
2 hours	81·7%	5 ,,	103·6%
3 ,, ...	87·8%	6 ,,	108·5% = 2·5 mols. C_3H_6/1 mol. H_2SO_4

The weight increases are low on account of loss of SO_2 and also probably of small amounts of paraffins and isopropyl alcohol.

A second experiment was made using only 1 c.c. of sulphuric acid. The increases were :—

3 hours	134%
6 ,, ...	162%
10 ,, ...	185%
17 ,, ...	209% = 4·87 mols. C_3H_6/mol. H_2SO_4

On dilution and extraction with ether 0·87 gms. of total hydrocarbons were obtained=47 per cent. on the weight of acid taken. An attempt was made to determine the amount of alkyl sulphate present by conversion to the barium salt, but it was found that though much was formed this decomposed steadily during the evaporation of the solution, barium sulphate being deposited and isopropyl alcohol escaping.

The very large increase in weight recorded above can only be explained by the formation of free isopropyl alcohol which suggests that hydration of propylene to the alcohol could be carried out continuously by feeding propylene and water under the correct conditions to sulphuric acid.

Some 50 c.c. of the paraffins were prepared by bubbling propylene into sulphuric acid and separating the top layer of oils. This had the following characteristics :—

d	20° C.	= 0·7607	
n_D	20° C.	= 1·4263	
r_L		= 0·3370	
mol. wt.		= 196	calc. for C_{14} H_{30} 198
Analysis	C	= 84·5%	C = 84·7%
	H	= 15·5%	H = 15·3%

Engler distillation :—

Drop	97° C.	Bromine absorption (Hanus) = 3·8%
25% over	@ 185° C.	
50% „	@ 220° C.	
75% „	@ 259° C.	
92% „	@ 300° C.	

The specific refractivity and the analysis indicate this material to be open chain paraffins. On boiling with sodium there was no action.

The following experiments were made in a small Drechsel bottle standing in tap-water using 10 c.c. of sulphuric acid of 98·5 per cent. strength. The paraffins were shaken out with light petroleum ether (b.p. < 40 C) which was distilled off on the water bath finally raised to boiling. The acid was then diluted with water to about 100 c.c. and the oils thrown out extracted with petroleum ether. The separation of oils was apparently never quite complete in this operation, since in the next stage (neutralisation with caustic soda and distillation) traces of oil were always carried over into the distillate. A measured volume of distillate was collected, filtered, and the amount of isopropyl alcohol determined by the refractive index of the filtrate. The following figures were obtained, compared with the weight of the acid employed :—

	Increase Per cent.	Paraffins Per cent.	Acid Wash Oils Per cent.	Isopropyl Alcohol Per cent.
a ..	7·2 ..	3·2 ..	3·1 ..	very small
b ..	15·2 ..	7·1 ..	6·8 ..	0·8
c ..	24·7 ..	9·6 ..	10·4 (mol. wt. 266)	7·9
d ..	28·4 ..	10·9 ..	12·3 ..	8·1
e ..	34·5 ..	12·4 ..	12·3 ..	11·3
f ..	61·4 ..	20·4 ..	20·7 ..	10·7

Expt. (d) Mixture heated to 30° C. for ½ hr. before analysis.

With regard to the acid wash oils these appear to be very similar to those from isopropyl alcohol (*vide seq*). They are light in colour when freshly prepared but darken rapidly on exposure to air and become thick and gummy in time. They are of high density and refractive index and absorb large amounts of bromine.

(3) *Amylene.*—The amylene employed was prepared by passing the vapour of fusel oil (125—135° C.) over phosphoric acid on pumice heated to 400° C. The following fraction was taken :—

bp.	33—37° C.	Probably chiefly trimethylethylene.
d 15° C. ..	0·6611	
n_D 15° C. ..	1·3871	

Bromine absorption 233 per cent. (Hanus).

200 c.c. of this amylene was run under vigorous stirring into 600 c.c. of sulphuric acid 98 per cent. strength, the temperature

being kept below 20° C. On standing overnight 120 c.c. of oils separated :—

d 15° C. .. .. 0·7641
n_D 15° C. .. .. 1·4362
Bromine absorption 4·2 per cent. (Hanus).
Analysis .. .. C=84·1%
H=15·7%

Fractionated through a plain tube, 60 cms. long gave the following figures :—

Drop	91° C.	50 per cent. ..	215° C.
10 per cent. ..	145° C.	60 „ ..	232° C.
20 „ ..	163° C.	70 „ ..	263° C.
30 „ ..	180° C.	80 „ ..	301° C.
40 „ ..	198° C.	90 „ ..	353° C.

The distillation above 232° C. was carried on in an Engler flask. The following fractions were collected and examined :—

No.	°C.	Bromine absorption. Per cent.	d 15° C.	n_D 15° C.	r_L
1.	To 163	0·2 ..	0·7194 ..	1·4078 ..	0·3428
2.	„ 198	0·3 ..	0·7467 ..	1·4203 ..	0·3391
3.	„ 232	0·6 ..	0·7679 ..	1·4350 ..	0·3398
4.	„ 301	4·1 ..	0·7925 ..	1·4471 ..	0·3372
5.	Residue	9·6 ..	0·8207 ..	1·4616 ..	0·3347

The specific refractivities of the fractions point clearly to their being chiefly open chain paraffins. This is confirmed by the elementary analysis of the original top layer before fractionation.

The acid layer on dilution gave about 40 c.c. of dark heavy oils. This, steam distilled, gave 12 c.c. of pale yellow oil having a somewhat turpentine-like odour :—

d 15° C. .. 0·8606 } r_L .. .. 0·3384
n_D 15° C. .. 1·4943 }
Bromine absorption 251 per cent. (Hanus).
Mol. wt. .. 210 Distillation range about 150—300° C.

The bromine absorption and molecular weight point to this oil being a mixture of triolefines :—

Calc. for $C_{18}H_{24}$
mol. wt. 206
r_L 0·340

Further experiments were made with weaker acid[6] and with a mixture of equal volumes of amylene and benzene. 100 c.c. amylene plus 100 c.c. benzene with 600 c.c. of acid gave 43·5 c.c. of separated oil :—

d 15° C. .. .. 0·8001 } r_L=0·3519
n_D 15° C. .. .. 1·4750 }
Bromine absorption 1·8 per cent. (Hanus).
Distillation range 120° C. to 76 % over at 360° C.

The high density and refractivity indicated that phenyl groups had gone into the separated oil. Further shaking with 98 per cent. acid failed to dissolve anything more.

(4) *Higher olefines.*—Experiments made with narrow boiling range fractions from a "cracked" petroleum spirit showed that the action of sulphuric acid was in all cases to yield large amounts of saturated hydrocarbons of high boiling point. These hydrocarbons appeared to be chiefly open chain paraffins.

Alcohols.—Methyl and ethyl alcohols do not appear to form hydrocarbons.

Isopropyl alcohol.—The alcohol used was fractionated from Howard's absolute "Avantine" :—

b.p.	.. ..	81·6—82·0° C.
d 20° C.	.. ..	0·7867
n_D 20° C.	.. ..	1·3776

In general in the following experiments 100 c.c. of alcohol was dropped slowly, with stirring, into 500 c.c. of sulphuric acid, keeping the temperature below 25° C. by tap-water cooling. Sometimes separation of paraffins occurred immediately, but in some cases the final mixture was clear and the paraffins were thrown out on overnight standing. The separation was observed to commence in one case and it was found the temperature had risen from room temperature (20° C.) to 25° C. The separated paraffins were tapped off and weighed. The strong acid liquor was extracted with the light petroleum which usually gave a small amount more of the same paraffins as shown by the appearance, saturation and refractive index. An aliquot, usually 1/5 of the acid was then diluted with 5 volumes of water and the oils and isopropyl alcohol determined as under propylene :—

(*a*) { 100 c.c. isopropyl alcohol
500 c.c. 98·5 per cent. H_2SO_4

Paraffins. 32·40 gms. = 41·3 per cent. on wt. of alcohol

d 20° C. 0·7642 } r_L = 0·3365
n_D 20° C. 1·4278 }

		Calcd. for $C_{18}H_{38}$
Mol. wt. 212		
Analysis	C = 84·9%	84·9%
	H = 15·1%	15·1%
Bromine absorption (Hanus)		2·6%

No action with metallic sodium was observed.

Acid wash oil 24·20 gms. = 30·8% on wt. of alcohols.

d 20° C. .. .. 0·9025 }
n_D 20° C. .. .. >1·5 } These oils were dark and viscous.
Mol. wt. .. .. 260 }

Bromine absorption (Hanus) 184%

Analysis .. .. C = 81·4% S = 3·1%
H = 12·7% O = 2·8% by diff.

Isopropyl alcohol. 0·13 gms. = 0·2% on wt. of alcohol.

It may be noted that the carbon content of the paraffins, wash oils and the small residue of unchanged alcohol is 60·1 per cent. of the weight of alcohol employed. The latter contains 60·0 per cent. of carbon. It may be inferred therefore that the paraffins and acid wash oils constitute the whole products of the reaction.

(*b*) An earlier experiment in which the mixture was warmed to about 50° C. before tapping off the paraffin layer :—

Paraffins. 27·9 gms.=35·0% * on wt. of alcohol.
d 20° C.=0·7717 } r_L=0·3357
n_D 20° C.=1.4315 }
Bromine absorption (Hanus) 2·0%
Engler distillation.
Drop 117° C.
20% over @ 196° C.
40% „ @ 219° C.
60% „ @ 240° C.
80% „ @ 267° C.
92% „ @ 300° C.

(*c*) Mixture and procedure as in (*a*) except acid 95 per cent. strength :—

Paraffins. 32, 44 gms.=41·4% on wt. of alcohol.
d 20° C. 0·7808
n_D 20° C. 1·4354
Mol. wt. 210
Bromine absorption (Hanus) 6·5%

The 40 c.c. of oils were shaken with 10 c.c. of the 98·5 per cent. H_2SO_4. The loss appeared to be less than 1 c.c. and the bromine absorption dropped only to 5·4 per cent. The wash acid was dark in colour.

Acid wash oils.—20·6 gms.=26·2 per cent. on alcohol used.

Isopropyl alcohol.—0·28 gms.=0·4 per cent.

(*d*) Mixture as (*a*), but acid strength 102·6 per cent. H_2SO_4.

Much SO_2 was evolved during the alcohol addition. Only traces of paraffins were found and small amounts of acid wash oils and isopropyl alcohol.

(*e*) 100 c.c. isopropyl alcohol.
125 c.c. sulphuric acid 98·5 per cent. strength.

Only 5·5 gms. of paraffins separated overnight. On adding a further 125 c.c. acid and standing again 5·5 gms. more oil separated. The addition of P_2O_5 brought about a further small separation.

(*f*) 50 c.c. isopropyl alcohol.
250 c.c. sulphuric acid 98·5 per cent. strength.

The mixture was kept below 20° C. during the alcohol addition and was clear when the latter was all in. An aliquot portion was

* Acid not extracted with petroleum ether

analysed immediately after the running in of the alcohol which occupied 2 hours and again after 3 hours' stirring at 18° C. :—

	1st sample. %	2nd sample. %
Paraffins	4·6	4·6
Acid wash oils	29·9	44·4
Isopropyl alcohol	nil	nil

The acid wash oils in this case appear to be largely paraffins thrown out by the heat of dilution.

The stirring was now stopped and in a quarter of an hour paraffins began to separate. After all night standing the following amounts (calculated back to the original mixture) were obtained :—

Paraffins	16·06 gms. = 41·0 per cent.
Acid wash oils	8·0 gms. = 20·4 per cent.
Isopropyl alcohol	small

The nature of the highly unsaturated oils thrown out on diluting the wash acid cannot be regarded as definitely determined. The whole of the wash acid in a repetition of experiment (*a*) was steam distilled. This gave 10·3 gms. of yellow oil having a somewhat turpentine-like odour and the following characteristics :—

d 20° C. 0·8543
n_D 20° C. 1·4675
$r_L = 0·3251$
Mol. wt. 185.
Bromine absorption 221% (Hanus).
The residue in the flask was a soft sticky pitch.

In a further repetition of the same experiment the whole of the wash acid was diluted and shaken with petroleum ether. The petroleum ether layer was shaken with caustic potash solution. The colour of the ether layer was turned from a muddy green to a clear yellow. The oil after distilling off the ether was yellow and very viscous and showed :—

d 20° C. 0·9140
n_D 20° C. 1·4917
$r_L = 0·3172$
Mol. wt. 201.
Bromine absorption 238% (Hanus).

Both these oils appeared to contain some oxygen and to oxidise rather readily. The bromine absorption indicates that if they could be freed from oxygen and sulphur they would be found to be triolefines. Their reactive character, however, will make a determination of their exact nature somewhat difficult.

n-propyl alcohol.—Supplied by B. D. H. :—

d 20° C. 0·8049
n_D 20° C. 1·3854

100 c.c. was run into 500 c.c. 98·5 per cent. strength sulphuric acid with stirring and cooling. The following products were obtained :—

Paraffins—

29·39 gms. = 36·6%

d 20° C. 0·7623 } r_L = 0·3382
n_D 20° C. 1·4290 }

Bromine absorption 1·6% (Hanus).
Mol. wt. 198.

Wash acid oils—

19·55 gms. = 24·4%.

Alcohol—

2·0 gms. = 2·5%.

Amyl alcohol.—The alcohol employed was a middle fraction collected 129—130° C. from amyl alcohol of B.P. quality.

(*a*) 100 c.c. alcohol 500 c.c. sulphuric acid 98·5 per cent. strength.

Paraffins.—37·7 gms. = 46·7 per cent. on alcohol used :—

d 20° C. 0·7447 } r_L = 0·3386
n_D 20° C. 1·4183 }

Mol. wt. 178	Calcd. for $C_{12}H_{26}$
Analysis C = 83·8%	Mol. wt. 170
H = 16·1%	C = 84·7%
	H = 15·3

Bromine absorption 1·0% (Hanus).

Engler distillation

Drop 64° C.	
20% over @ 158° C.	60% over @ 213° C.
40% " " 186° C.	80% " " 248° C.
	95% " " 300° C.

Acid wash oils.—24·3 gms. = 30·0 per cent. No alcohol could be traced in the diluted acid. The elementary analysis of the paraffins appeared to be unsatisfactory, so that a second lot of paraffins was prepared. These showed :—

d 20° C. 0·7415 } r_L = 0·3329
n_D 20° C. 1·4083 }
Analysis C = 84·2%
H = 15·4%

The hydrogen content is thus of the correct value. An oxygen content of 0·4 per cent. is shown by difference which accounts for the lower r_L value.

(*b*) 100 c.c. amyl alcohol
100 c.c. sulphuric acid 98·5 per cent.

gave only 2·8 gms. of paraffins. The residue was distilled from water bath. A vigorous reaction ensued, much SO_2, fatty acids and aldehydes being evolved, but only a trace of paraffins. A large residue of carbon char was left in the flask.

Cyclohexanol.—The cyclohexanol employed was a middle fraction of the commercial product m.p. = 19° C. :—

100 c.c. cyclohexanol
500 c.c. sulphuric acid 98·5%

Gave 34·5 gms. top layer of oils=36·8 per cent. on wt. of alcohol used :—

d 20° C. 0·9029
n_D 20° C. 1·4888 } r_L=0·3196

Mol. wt. 253
Bromine absorption 1·6%
Analysis .. C=86·5%
H=13·5%

Calcd. for $C_{18}H_{34}$
250
86·4%
13·6%
r_L=0·3232

Engler distillation.
Drop .. 208° C.
20% over @ 257° C.
36% „ „ 300° C.

These oils were colourless and notably viscous, and had an odour strongly resembling deca-hydronaphthalene.

The specific refractivity and the analysis indicate a large proportion of bicyclic naphthenes. It may be of interest to note that these oils strongly resemble the corresponding fractions from the natural "freak" Badapur oil.[7]

O-methyl cyclohexanol :—

d 20° C. 0·9289
n_D 20° C. 1·4660

Gave 34·5 per cent. of colourless mobile oils :—

d 20° C. 0·8313
n_D 20° C. 1·4545 } r_L=0·3261
Bromine absorption 0·8% (Hanus).
Mol. wt. 161.
Acid wash oils 50·5%.

m-methyl*cyclo*hexanol :—

d 20° C. 0·9169
n_D 20° C. 1·4579

Gave 32·8 per cent. of colourless mobile oils :—

d 20° C. 0·8270
n_D 20° C. 1·4535 } r_L=0·3272
Bromine absorption 1·0% (Hanus).
Mol. wt. 157.
Acid wash oils 50·6%.

p-methyl cyclohexanol :—

d 20° C. 0·9178
n_D 20° C. 1·4222

Gave 33·6 per cent. of colourless mobile oils :—

d 20° C. 0·8274
n_D 20° C. 1·4525 } r_L=0·3263
Bromine absorption 0·5%.
Mol. wt. 160.
Acid wash oils 51·3%.

The acid wash oils from the three methyl cyclohexanols were bright green in colour, but turned yellow on washing with caustic potash solution.

In addition to the bodies already mentioned qualitative experiments indicate the production of paraffins from

n-butyl alcohol
iso-butyl alcohol
amyl acetate.

Some experiments are in progress with alcohols of high molecular weight, e.g. cetyl, myricyl. The results already obtained indicate that paraffin wax is obtained by the action of the acid. The yields so far are low, but this is probably due to certain experimental difficulties experienced in attempting to carry out the reaction with these solid alcohols.

Summary.

Both olefines and alcohols in the presence of an excess of concentrated sulphuric acid form saturated hydrocarbons separating from the mixture and highly unsaturated bodies remaining in acid solution. Alcohols and olefines derived from open-chain paraffins give open-chain paraffins, whilst alcohols from cyclic paraffins yield cyclic and polycyclic paraffins.

When olefines and aromatics are brought together into contact with strong cold sulphuric acid some of the aromatics join with the separated paraffins.

The authors wish to acknowledge the financial assistance received from the Distillers Company, Limited, and the Fuel Research Division of the Department of Scientific and Industrial Research towards the expenses of this research.

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Motor Spirit, with Special Reference to its Use in Internal Combustion Engines.*

By H. Y. V. Jackson, M.C., M.Sc.(Tech.), A.M.I.Mech.E., A.M.I.E.E. (Member).

Introduction.

The most usual form of motor spirit is a petroleum derivative known by various names such as petrol in England, gasoline in America, essence in France, benzine, naphtha, etc., and petroleum refiners are usually faced with the problem of manufacturing such a spirit to very rigid specifications. The relation between these specifications and the actual use of the spirit in internal combustion engines is clouded in a certain amount of mystery, and the object of this paper is to elucidate the correlation between the specification for a spirit and its actual behaviour in a motor, and to discuss in a general way the design and operation of engines required to run on such spirits. The paper will be confined chiefly to petroleum spirit, although the use of other light fuels will be touched upon. Unless otherwise stated, the words motor spirit will refer to a petroleum derivative.

It is advantageous for a constant liaison to be maintained between the engine makers and the oil refiners, in order to effect the most economical and satisfactory compromise. The present paper discusses the points which arise in endeavouring to obtain this object, and suggestions will be put forward for improving both the engine and the spirit.

Before discussing the properties of motor spirits, the design, construction and operation of the usual modern engines which run on such spirits were briefly reviewed.

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* Paper read before the Persian Branch of the Institution of Petroleum Technologists on September 28th, 1927.

It can be demonstrated mathematically that any engine with a number of cylinders in line which is a multiple of three, can be dynamically balanced practically perfectly, whereas two, four, eight cylinders, etc., in line cannot be perfectly balanced. Actually in practice, however, the balance characteristics of the latter class when the engine is properly designed are not noticeably different from the former class.

Timing.—In a survey of the operations of a four cycle engine it appears that the inlet and exhaust valves open and close at the beginning or end of a stroke and that the mixture is fired at the top of the power stroke. In actual practice due to various considerations, the setting of the cams is such that a lag or lead is given to the opening and closing of valves, and ignition is as a rule advanced to take place before the piston reaches the top of the power stroke. The exhaust valve is always given lead in opening and lag in closing to enable the burnt gases to be cleared out of the cylinder as effectively as possible. The inlet valve is given lag in opening and closing. The lag in opening is to avoid any possibility of the burnt gases passing back into the induction pipe and so retarding the incoming fresh mixture, and the lag in closing is to take advantage of the inertia of the rapidly moving incoming mixture to slightly increase the charge in the cylinder. There is a time lag between the passing of the spark and the actual point of maximum pressure in the cylinder, so that the spark is advanced to ensure that this pressure is reached when the piston is at the top of its stroke. The amounts of lead, lag, and advance depend on the design of engine, but in general they all increase with increase of speed. The properties of the fuel also have an important bearing on these amounts, as will be seen later.

Motor Spirit.

A review of the various operations in an engine as briefly discussed above indicates that the ideal fuel should have certain characteristics which will be discussed as follows:—

Volatility.—As the liquid fuel has to be converted into a vapour in a very short space of time without, if possible, the application of heat, it is obvious that the higher the volatility the easier this conversion is brought about. As stated previously the spray action of the carburettor jet introduces minute droplets of spirit into the induction pipe of the engine. This fine mist suspended in a comparatively large volume of air, results in the exposure of

an enormous surface of liquid to the air, and if the boiling point of the liquid is low, rapid evaporation takes place. By the physical law of partial pressures, the pressure of the petrol vapour in the mixture of air and petrol, is only some fraction of the total pressure of the mixture depending on the relative proportion by volume of petrol vapour present in the mixture. For instance, the total pressure of the mixture in the induction pipe of the engine will be somewhat less than atmospheric due to the suction effect of the engine. Assuming this figure is 10 lbs. per sq. in. and the proportion of petrol vapour is 2 per cent. by volume of the mixture, then the actual pressure in the petrol vapour is 2 per cent. of 10 lbs. or 0·2 lb. per sq. in. Under this low pressure and at atmospheric temperature the petrol must remain a vapour. This explains why, after the initial vaporisation and mixture with air takes place, the petrol will not condense out again however long the mixture remains standing before combustion occurs. Unless heating arrangements are provided, which introduces complications into an engine, especially at starting, it is obvious that the inital boiling point of the spirit used should be as close to atmospheric temperature as possible. On the other hand an inflammable liquid which boils at atmospheric temperature would be a dangerous and costly one to handle. The losses would be very great as evaporation would be proceeding rapidly whenever the spirit was exposed to air. This is one of the reasons why a spirit consisting of one pure chemical compound with a definite fixed boiling point is not suitable for internal combustion engine work. If the boiling point is low, danger and loss are incurred in handling. If the boiling point is high, difficulties are experienced in vaporising the liquid before introduction to the engine. We now, therefore, come to one of the chief reasons why petrol is such a suitable spirit. Petrol is a mixture of hydrocarbons obtained by the distillation of crude oil, which itself is a mixture of hydrocarbons. The constituents of the crude oil consist of hydrocarbons varying from heavy complex waxy substances which are solid at ordinary temperatures to light fractions such as methane, ethane, etc., which are gaseous at ordinary temperatures. Petrol is a mixture of the hydrocarbons situated at the light end of this scale. It is very essential in considering vaporisation and carburettor problems always to bear in mind the fact that petrol is a mixture of a series of hydrocarbons each with its own separate boiling point. To illustrate this, the following are the constituents of a simple motor spirit consisting of hydrocarbons of the paraffin series, and apart from impurities and some more complex substances such as sulphur bodies, aromatic compounds, etc.. may be taken as representative of the ordinary

spirit sold on the market as petrol. The boiling points and specific gravity of each constituent are given :—

MAIN CONSTITUENTS OF AN ORDINARY PETROL.

Substance.	Chemical formula.	Molecular weight.	Boiling point. At atmospheric temperature and pressure. °C.	°F.	Specific gravity.	Remarks.
Methane ..	CH_4	16	—164	—263	0·55 (Air = 1)	These fractions are gaseous at atmospheric temperature and pressure
Ethane ..	C_2H_6	30	— 84	—119	1·04 (Air = 1)	
Propane ..	C_3H_8	44	— 37	— 35	1·56 (Air = 1)	
Butane ..	C_4H_{10}	58	0	32	2·05 (Air = 1)	
Pentane ..	C_5H_{12}	72	36	97	0·645 (Water = 1)	
Hexane ..	C_6H_{14}	86	69	159	0·677 (Water = 1)	These fractions are liquid at atmospheric temperature and pressure
Heptane ..	C_7H_{16}	100	98	208	0·709 (Water = 1)	
Octane ..	C_8H_{18}	114	120	248	0·707 (Water = 1)	
Nonane ..	C_9H_{20}	128	150	302	0·755 (Water = 1)	
Decane ..	$C_{10}H_{22}$	142	173	343	0·747 (Water = 1)	

It will be understood of course that these are only the simpler constituents of an ordinary petrol. Actually the composition of the individual hydrocarbons is much more complex, but these figures serve to illustrate the problems we are now discussing in connection with the behaviour of such a fuel in the carburettor. The proportions of these constituents vary with the brand of petrol and the particular crude it is derived from. Generally, however, the gaseous fractions only total a few per cent. It will be realised that these fractions are only gaseous when isolated at atmospheric temperature and pressure. When they exist in the mixture known as petrol, they are in solution, the amounts of each which will dissolve in the remaining mixture being a function of their molecular weight and increasing with the latter. A further point is that all the fractions, liquid or gaseous, although they are distinct separate chemical compounds, are all so closely related as regards their chemical and physical properties, being merely gradations in the hydrocarbon series, that the only effect of mixing them in different proportions is to alter the gravity and boiling points of the mixture.

Now let us consider what happens when a petrol consisting of a mixture of substances as described above is vaporised. By a well-

known physical law the boiling point of a liquid—*i.e.*, the temperature at which it vaporises when equilibrium is established between the liquid and the vapour (or mixture of vapour and air) above it, is dependent on the pressure, increasing with the latter. The petrol can be vaporised in two ways therefore, either by heating it or reducing the pressure on it. Supposing a sample of petrol be heated then at a given temperature so much vapour will be given off, but the important point to remember is that this vapour still contains proportions of each of the original constituents of the petrol, but the proportion of the lighter constituents is greater than in the case of the original mixture. As the temperature is raised the resulting vapour will contain at first an increasing and subsequently a decreasing proportion of the heavier constituents, until finally at a certain temperature the whole of the petrol including the heaviest ends will be vaporised, and the composition of the vapour will be the same as that of the original liquid except for small losses of some of the gaseous fractions. If the vapours given off at each temperature are condensed, and the volumes of this condensate, as a percentage of the original volume of the spirit are plotted against temperature we obtain the usual characteristic distillation curve for the spirit, known colloquially as an "Engler" because of the method of obtaining it by distillation according to Engler's procedure.

Starting and Acceleration.—The main advantage of a low initial boiling point is ease of starting. Let us imagine the conditions in an engine when starting after being shut down for some period, more especially in a cold climate. Firstly, the lubricating oil, which has formed a film over all the working parts of the engine, will be cold and therefore comparatively viscous. This increases the torque required to turn the engine over, putting a strain on the electric self-starter and battery where fitted or causing very often considerable arm ache and loss of temper when hand starting is used. It will be of interest to know that in an ordinary automobile engine of 24 h.-p. on a cold morning the starting current required in an electric starter is often in the neighbourhood of 150 amperes at 6 volts representing nearly 1¼ h.-p. Any properties of the spirit which will enable the engine to start quickly are therefore obviously to be recommended. Considering the conditions in the carburettor and induction pipe, these are also far from ideal at starting. The petrol oozes through a cold jet, feebly assisted by the suction of the slowly turning engine. A certain amount of mist or fine spray is formed which, due to the low velocity in the induction pipe, settles as a film on the walls of the latter, and before the air-contact time factor can produce a sufficiently rich mixture to fire in the cylinders the engine has been turned several revolutions. The spectacle of an

irate motorist spinning his engine with the self-starter on a cold morning without the slightest sign of the engine firing is a familiar one to everybody in modern times, and testifies to the sturdy construction of present-day starters and batteries. Now with a low initial point petrol, a small amount will be evaporated after passing the jet even in the coldest weather, and by closing the choke the full suction effect of the engine is brought to bear on the jet which assists vaporisation by reducing the pressure. Further, cutting off the air in this manner enables a combustible mixture to be formed even if the quantity of spirit evaporated is small. It follows also from the point of view of engine starting that the distillation curve for the petrol should rise slowly at first—*i.e.*, a small increase in temperature should effect the evaporation of a goodly proportion of the spirit. On the other hand, if the initial boiling point is too low, and the rate of rise of the curve too small, considerable losses will be incurred is using the fuel, especially in warm weather or in hot climates. One can imagine, for instance, that petrol with an initial point of say 100° F. lying in a tank at the rear of an automobile in a country with a sun temperature of 120° F. (which is not excessive) will be subject to a good deal of loss. The small initial steepness in the curve is an advantage in this respect as it allows a small margin between the low initial boiling point and the slightly higher temperatures at which evaporation becomes more rapid. Further, under the influence of the suction of the engine, with high temperatures around the carburettor gas locks are liable to form in the latter. When it is considered that the rate of flow of a fuel in a gaseous form through a carburettor jet is only in the order of 1/1000 of that when the fuel is liquid, it will be realised that if a gas lock occurs in a carburettor the engine will stop. This has no doubt been the cause of many engine failures and disastrous accidents in aeroplanes, as aviation fuels have lower initial boiling points, and the petrol is as a rule pressure fed to the carburettor. With the auto-vac feed the problem is not so serious as the spirit is subjected to the full engine vacuum in the auto-vac before reaching the carburettor and a vent is provided to allow for the escape of any gases which accumulate. The author is of the opinion that one of the reasons for the superior starting properties of a modern auto-vac fed automobile engine over the old type engine with a hand pump on the dash-board for maintaining pressure in the fuel tank is this absence of gas locks in the carburettor with the former.

Closely allied with the question of starting is that of acceleration, especially in automobile engines. After the engine has fired, the choke is opened and the full volume of air is allowed to enter the carburettor to produce as lean a mixture as possible consistent with even firing and power production. In most engines the

carburettor design is such that the correct fuel-air ratio is more or less maintained automatically after the engine has started. Now it takes some little time for the whole engine to warm up, and as the requirements of a modern automobile are often such that once the engine has started, the driver should be able to "step on the gas" and quickly accelerate a heavy vehicle weighing 2 tons from rest to 40 miles per hour in 15 to 20 seconds, bringing enormous inertia loads on the engine, it behoves us to enquire into the behaviour of the fuel in the carburettor under these conditions. While accelerating in this fashion, the throttle is naturally nearly full open, and therefore the full suction of the engine draws large quantities of fuel through the jet and air through the air intake. Unless the volatility of the fuel is high, the mist which is formed impinges on the walls of the still relatively cold induction pipe and forms a film there. Only the lighter fractions evaporate, especially as the time factor for equilibrium between the liquid fuel and the vapour in contact with it to be established is relatively small, due to the increasing speed of the engine. Hence from an acceleration point of view a distillation curve which rises slowly is desirable. It will be shown later that the criterion of a good spirit in this respect is the amount distilled off up to 212° F., as it is the volatility below this temperature which has an important effect on the starting and acceleration of the engine—*i.e.*, during the period when the engine has not warmed up sufficiently to ensure complete vaporisation of the fuel in the induction pipe. In practice, small differences in volatility make very appreciable differences to the performance of the engine in this respect. A very comprehensive series of tests has recently been made in America to discover how the starting and acceleration properties of a fuel can be correlated with its distillation curve. These tests were performed independently by the U.S.A. Bureau of Standards (Mr. J. O. Eisinger) and by Dr. Brown in a very complete research at Michigan University. The tests were made on actual commercial automobile engines with no special adjustments, and the starting properties were measured as the time or number of revolutions of the engine between the turning on of the fuel and the first explosion.

A study of these various tests and consideration of the behaviour of the fuel in a carburettor definitely show :—

(1) That the starting and acceleration properties of a spirit are dependent on the percentage distilled off as follows :—

At 80° F.	by the	percentage	distilled	off	at	..	250° F.
„ 70° F.	„	„	„	„	„	..	200° F.
„ 35° F.	„	„	„	„	„	..	150° F.
„ 10° F.	„	„	„	„	„	..	100° F.

and that the actual percentage off at these temperatures should be at least 20 per cent. and preferably up to 30 per cent.

(2) Neither end point nor gravity has any effect on the starting or initial acceleration of the engine.

70° F. represents an average temperature in temperate climates such as England or U.S.A., and it is a fact worth noting that ordinary English straight run petrols give 34 per cent. over at 200° F., and are therefore much superior for "liveliness" to the average straight run American gasoline with only 18 per cent. over at 200° F. In America difficulty is experienced in starting cars in the winter with a temperature of 32° F., and there is a good deal of agitation on foot to market specially volatile fuels for the winter.

The first problem refiners have to face is, therefore, to produce a spirit with high volatility at the lower end of the curve. Unfortunately this desirable feature clashes with the economics of petroleum refining, because if the cuts from the crude are too light the quantity of spirit produced is reduced and refiners are left with a lot of unmarketable heavy fractions on their hands ranging from heavy naphthas to light kerosines. The tendency has always been therefore, until quite recently, to cut as deeply into the crude oil as possible consistent with making a spirit which will vaporise in an ordinary carburetter. American gasolines are particularly heavy compared to the petrol marketed in England, and have correspondingly poor starting and acceleration properties. Comparative distillation curves for an average American and an average English straight run aviation spirit show how much more volatile the latter is.

Now there are two ways of obtaining a spirit which will give greater volatility up to 212° F. and therefore better starting and acceleration properties, namely:—

(1) To cut less deeply into the crude, producing a spirit with better volatility all along the curve. This product will then virtually become an aviation spirit. The disadvantages of this method are as stated before, that the yield is reduced and a quantity of heavy ends are left which are difficult to dispose of. Refiners reached their limit in this direction some time ago, and there was little hope of improvement on the straight run products already on the market.

(2) By blending natural gasoline with a low volatility straight run spirit. Natural gasoline is a low gravity high volatility spirit extracted by well-known processes from the gas which is obtained from oil wells known as casinghead gas. This gas is composed of the lighter ends of the same petroleum series as the crude oil,

and the properties of the extracted natural gasoline are, except for lower gravity and higher volatility, practically identical with the motor spirits distilled from the crude. This natural gasoline contains, of course, a greater proportion of the lighter ends of the hydrocarbon series than a normal motor spirit—*i.e.*, the methane, ethane, propane, butane, etc., constituents are more in evidence. The gasoline is very "wild"—*i.e.*, volatile—and would result in great losses if used by itself in internal-combustion engines. By adding it to a heavier straight run spirit, however, in the right proportion, the volatility of the former can be increased at the beginning of the curve without seriously interfering with the properties of the resultant spirit further up the curve. The heavy spirit (naphtha) is a refinery product not volatile enough for a motor spirit but too light for mixing in with a kerosine. The natural gasoline is a product extracted from still gases. The properties of this gasoline are similar to those of casinghead gasoline. A two to one blend of naphtha with gasoline gives a product which is much more volatile than ordinary standard petrol at the lower end of the curve but is less volatile at the upper end. Such a spirit is a little too light. Its loss in handling would be high, and also its reduced volatility at the upper end of the curve would retard complete vaporisation in the engine. By blending, however, straight petrol with this blend in the ratio of two to one, a spirit is produced which is a little more volatile up to 212° F., without being seriously different from the straight product further up the curve.

It is thus seen that by using two products, naphtha and light gasoline, neither of which are very much used on the market when considered separately, a 50 per cent. increase in yield of motor spirit is obtained, and this spirit is superior in its starting and acceleration characteristics to the straight run product. In practice such large yields are not realised as various losses occur, and it is not always possible to obtain the naphtha and gasoline in the required proportion. It is now, however, possible, and is general practice in America to make motor spirits with very much better volatilities at the lower end of the curve and at the same time increase the yield by 25 per cent. Twelve per cent. of all the petrol marketed in the United States is made in this manner by blending heavy straight run spirits with natural gasoline extracted from casinghead gas. The American motor spirits so made approach very much closer at the lower end of their curves to the English petrol. English petrol, as previously pointed out, is actually the best on the market from the point of view of engine starting and acceleration, but unless it is produced by blending methods as previously described, it is only available at the expense of

reduced yields and a residue of unsaleable products with consequent financial loss to the refiner.

In practice the addition of more than 20 per cent. of natural gasoline is not recommended as the fuel is reduced in gravity and the upper part of the distillation curve is affected too much.

It might be mentioned here that it has been proposed that as an Engler distillation does not represent the conditions of vaporisation in a carburettor that some other method of testing fuels should be standardised. The air distillation method used by the Bureau of Mines consists of passing known mixtures of air and vapour over a coil maintained at given temperatures by water, and measuring the amount of liquid which condenses out. The trouble is, however, that to get consistent results equilibrium must be reached between the liquid and vapour, and in an engine induction pipe the time element is so short that equilibrium is never obtained. These alternative methods are, however, worth pursuing.

Having now pointed out the duties of the refiner in connection with producing a spirit with reasonable starting and acceleration properties, it is not fair to let the engine designer go scot free, and it will be convenient at this stage to discuss any special engine features which will tend to get the best results from the fuel the refiner has gone out of his way to provide.

A series of very interesting tests has recently been completed by a Joint Committee of the U.S.A. Bureau of Standards, the American Petroleum Institute and the Society of Automobile Engineers. These tests bring to light a good deal of information regarding the starting properties of an automobile engine in relation to various engine features. A standard motor truck engine was mounted on a stand and driven at a constant speed by external means. A plain jet was used instead of a carburettor and various air-fuel ratios were obtained by varying the flow of fuel to the jet whilst maintaining a constant flow of air. The measure of the starting properties of the engine was taken as the time interval between turning on the petrol and the first explosion.

These tests all indicate that the important question in connection with reducing the starting time for a petrol engine is to get the correct mixture for firing into the cylinder head, as soon as possible, and they show that some of the factors in engine design which tend to promote this end are :—

(*a*) High cranking speeds.
(*b*) Efficient atomising jets in carburettors.
(*c*) High ratios of compression.

The tendency of modern engine design is to improve all these factors. In automobile work higher cranking speeds have been attained by larger electric self-starters and more robust battery construction. Carburettors have been improved by various means, the chief of which is the employment of two jets. One is a fine atomising jet which is used for starting and the other is a large jet which only comes into play when the throttle is opened wide to put the engine on load. Ratios of compression are showing a tendency to increase. Besides improving the starting properties of the engine, as previously shown, a higher ratio of compression means a higher efficiency. Unfortunately other troubles follow high compressions which we will refer to later.

With regard to improving the rapidity of vaporisation in the induction pipe of an engine, it is sometimes thought that manifold heaters, *i.e.*, muffles around the induction pipe through which the exhaust gases pass, will be effective in this respect. A little thought will show, however, that several revolutions of the engine must take place *after firing* before any heat is available at all. The same remarks apply to systems where the air is heated by the exhaust before passing into the carburettor. The author believes, however, that there is a good deal of scope for an electric heater operated from the battery and situated just above the carburettor jet so that the mist from the latter will impinge on it. Such heaters are already on the market, and it appears that a more extensive use of them would improve the starting of engines considerably even with the less volatile fuels.

Conditions in the Engine Under Load.

After the engine is started and has warmed up, the desirable features in the fuel are very different from those when starting. The problem now is to get as much heat energy into the cylinders as possible from the fuel. The calorific value of petroleum spirits in B.Th.U. per lb. decreases as the specific gravity increases, so that approximately the available heat per gallon is the same for any spirit. This brings to notice an interesting difference between fuels for automobiles and those for aero engines. A motorist buys his petrol by the gallon so that other considerations being equal the specific gravity of the spirit is immaterial. An aviator, on the other hand, requires maximum calorific value per unit weight, so a low specific gravity spirit is more advantageous to him. In view of the fact that the gravity and therefore the heavy portions of a spirit are immaterial to a motorist, once his starting and acceleration demands have been satisfied by the percentage over at 200° F., it might reasonably be asked why these heavy ends

should be included at all. The answer is that the refiner benefits in this respect. As stated before, if the spirit produced from the crude oil consisted of light ends only with a very flat distillation curve, then the refiner would be left with a quantity of heavy ends which he would not know what to do with. It has been shown previously that the shape of the distillation curve above 200° F. and the end point of the spirit have no effect on the starting and acceleration characteristics of the engine, so that for the sake of a cheap fuel it pays to keep the latter part of the curve as high as possible. There are, however, disadvantages in regard to this which will be dealt with later.

For aero engines of course the lighter the fuel the better.

As the properties of the fuel above 200° F. make very little difference within limits to the performance of the engine, it will be convenient to examine at this stage how the efficiency, power and fuel economy characteristics of the latter are affected by design.

The improvements which can be effected in modern engines to give greater power and fuel economy characteristics, using the ordinary motor spirit, are :—

(1) Increasing the ratio of compression.
(2) Heating the air to the carburettor.
(3) Cooling the mixture before entering the cylinders.
(4) Supercharging the mixture by means of a blower.
(5) Long, large diameter induction pipes.

The last two methods are not standard practice at present, but there is a tendency with engine manufacturers to adopt them.

Knocking.—A problem which has arisen in the last few years, and which has caused a good deal of concern both to engine makers and petroleum refiners, is that known by various names (either correctly or incorrectly) such as knocking (pre-ignition), detonation, pinking, etc. It is a phenomenon associated with the combustion of the mixture in the cylinder head, and the symptoms are a metallic clicking noise which occurs in the cylinder when the engine is accelerated or put on load. During the last few years a considerable amount of work has been done by Ricardo and Prof. Callendar in England, Midgely, Kettering, etc. (General Motors, Ltd.), in America, the U.S.A. Bureau of Standards, and innumerable other investigators on the mechanism, effects, measurement and abolition of the knocking propensities of various motor fuels in different types of engines. Time and space forbid a detailed review of the mass of information now available on this problem, but a brief summary of the position to date will no doubt be of great interest, especially to those to whom the subject is a little mysterious.

Firstly, what is knocking? It has now been definitely demonstrated that knocking is entirely different from pre-ignition. Pre-ignition is merely the ignition of the charge in the cylinder by some irregular means, before the correct instant which is normally determined by the setting of the distributor. The effect of pre-ignition is the same as that caused by advancing the spark. The causes of it are usually: (*a*) Carbon deposit in the cylinder head. This can react in two ways. Firstly, the carbon takes up actual space which increases the compression ratio and, secondly, the heat flow to the outside of the cylinder is retarded. Both these effects result in high cylinder temperatures, and portions of the carbon may become so hot that the mixture is ignited on the compression stroke before the correct time. It is conceivable and probable that small sharp points of carbon become incandescent under these high temperatures and surface combustion effects are in evidence. (*b*) High compressions, with correspondingly high temperatures, together with inadequate cylinder cooling, may cause pre-ignition irrespective of the presence of any carbon.

As carbon is usually present even in small quantities, we may combine these two causes and say that pre-ignition is due to excessive temperatures inside the cylinder.

It is convenient at this stage to point out that the formation of carbon is due to incomplete combustion of the fuel and burning of lubricating oil, and the remedy for it is to use a fuel with the minimum of heavy ends and run with a mixture as lean as possible consistent with the engine developing its full power. A good quality lubricating oil is, also, of course essential.

The effect of pre-ignition is that the charge is fired and the pressure rises rapidly before the piston reaches the end of its compression stroke. The piston on completing this stroke thus compresses this high pressure charge to some higher pressure, and both the resultant pressure and temperature are higher than in the normal running of an engine. Conditions can actually be obtained in practice, especially in high compression aero engines, whereby if pre-ignition occurs very early in the stroke the net work performed on the piston is negative and the engine will stop. This is no doubt another explanation of many aero engine failures in mid-air.

The effect of this pre-ignition is cumulative—*i.e.*, once it occurs, the temperature of the carbon in the cylinder is raised further still, causing earlier pre-ignition on the next compression stroke, and so on until the power loss is so excessive that the load has to be reduced.

An important point to remember is that pre-ignition by itself does not cause the metallic noise known as knocking. In fact,

pre-ignition can be taking place without any noticeable external effects on the engine except loss of power and a certain harshness in running. The effect can be reproduced at any time by merely advancing the spark. Knocking is another phenomenon altogether, which is strictly defined as detonation. It is felt that a little further explanation on this point is necessary. When a mixture of air and a combustible vapour is ignited, although a so-called explosion takes place, actually a small though appreciable interval of time elapses between the instant of ignition and that when complete combustion takes place and the pressure is a maximum. This is normal combustion, and only varies in degree of rapidity from that of the ordinary burning of a flame in air. In the case of a mixture of petrol vapour and air, the time taken for complete combustion is in the order of 1/50 sec. Now consider an engine with a stroke, say, of 5 in. running at 1200 r.p.m., then the average piston speed is 200 in. per sec., and the piston completes a stroke in 1/40 of a second, so that the piston travels an appreciable portion of the stroke while combustion is taking place. The rate of combustion in the mixture depends chiefly on its richness. In practice with very lean mixtures it sometimes occurs that the mixture is still burning at the end of the stroke when the exhaust valve opens. The real point to consider is that at the pressures and temperatures pertaining in the cylinder of an engine towards the end of the compression stroke, the constituents of the fuel are so near the conditions required for oxidation that chemical combination commences before an actual flame is formed. The temperature of ignition is defined as the lowest temperature at which inflammation will take place, but the temperature of initial combustion (T.I.C.) is somewhat lower than this. A flame can only develop after initial combustion by a generation of heat so vigorous that the temperature rises rapidly before loss of heat can take place. Initial combustion can commence before a spark is passed, and as previously described it is assisted by the presence of carbon. When inflammation temperature is reached, the rate of combustion increases rapidly, and a pressure wave travels through the mixture with twice the velocity of sound. It is the reaction of this wave on the walls of the engine cylinder which produces the metallic noise known as knock.

An interpretation of what is actually taking place inside the engine cylinder has up to the present been very difficult. Some very excellent work has been done on the problem by the various scientific and manufacturing bodies in America previously referred to, and great ingenuity has been displayed in getting experimental verification of some of the various theories put forward. The practical demonstration of the anti-knock properties of various

fuels in actual commercial engines has also reached a high stage of development in America, but the author believes that the crux of the whole problem has at last been arrived at as the result of a most interesting research carried out by Prof. Callendar for the Air Ministry in England very recently. This research has done a great deal to elucidate the phenomena of detonation, and the liberty will be taken of quoting some of the conclusions arrived at.

Prof. Callendar conceived the idea that, as the mixture in the engine during the compression stroke was under thermal conditions approaching those when chemical combination of the fuel and oxygen in the air take place, a study should be made of the chemical properties of the mixture under these conditions. With this end in view he passed known mixtures of fuel and air continuously through glass tubes heated to various temperatures. The oxidation of the fuels was tested by a chemical examination of the products in various absorption tubes. In the glass tubes the actual combustion was visible, and it was also checked by the change in products. The temperature of initial combustion was registered in this manner for various fuels and various mixtures. On the same chart are given the final temperatures due to compression of the mixture for different ratios of compression. The large difference between the temperatures of initial combustion for benzene (which we know from practice is non-detonating in an engine) and pentane and hexane (which do detonate) will be noticed. A further point is that a detonating spirit such as hexane has an initial temperature of combustion below the normal temperature due to compression of the mixture, and that a non-detonating spirit such as benzene has initial combustion temperatures higher than those due to compression.

The theory of detonation now advanced as the result of these various investigations is as follows :—

Due to imperfections in the vaporising qualities of an ordinary carburettor, the heavier ends of a petroleum spirit remain in suspension as very fine drops in the mixture during compression. As the temperature of the mixture rises, due to compression, incipient oxidation (i.e., combustion) commences, the lighter ends of the spirit which are in the form of a vapour being consumed first. One of the results of the addition of the oxygen molecule to the hydrocarbon is the formation of alkyl peroxides which decompose into aldehydes and water. These peroxides are produced in greater quantities with a detonating fuel such as hexane than with a non-detonating fuel such as benzene. They are unstable compounds and detonate more or less violently when heated. They have been definitely isolated from the products of combustion resulting from the slow oxidation of the detonating

fuels as described above. Further an addition of these peroxides to a non-detonating fuel will cause it to detonate.

Now consider the conditions in an engine cylinder during compression. On the up stroke of the piston the mixture is compressed, and shortly a temperature is reached when slow oxidation commences. Unstable peroxides tend to be formed and as compression increases these are absorbed by the layers of pure unconsumed vapours in the immediate vicinity of the drops and finally condensed with them into the drops. If no drops are present to absorb the peroxides they decompose as quickly as formed, producing aldehydes and water. A further rise in temperature due to further compression and the heat of combustion from the intermixed burning vapour causes these peroxides to detonate. Each drop then becomes the centre of a minute explosion, the drop is disintegrated and vaporised, and combustion of the whole mixture is completed. It is the summation of these minute explosions which produces the metallic knock in the engine. Experiments were made with two combustion tubes in the same furnace, one through which the mixture was passed with the fuel completely vaporised, and one through which air containing the fuel as a fine mist was passed. The temperature of both tubes naturally was the same. The peroxides were formed to a much greater extent in the tubes containing a mist, and ignition, as shown by the flame produced, occurred at lower temperatures.

It has long been known that the addition of certain dopes to fuels will prevent this detonation, and the explanation of this also follows from the above research. Such dopes are usually organic metallic compounds such as tetra-ethyl lead, iron or nickel carbonyl, etc. These dopes also naturally concentrate in the nuclear drops referred to above, decompose, and deposit metal. These metallic deposits apparently prevent the absorption of the peroxides so that the latter cannot form so easily. This was proved also in the tube experiments by passing a pure 10 per cent. hexane mixture through one tube and a similar mixture containing lead ethide through the other. The undoped mixture produced aldehydes and water as products of combustion, being the results of the decomposition of the peroxides formed, while the doped mixture produced practically no aldehydes and water.

Having examined the mechanism of detonation and the effects of dopes on the fuel we can now consider the practical considerations involved.

Firstly, although as shown, pre-ignition and knocking are two distinctly separate phenomena, they are closely related to one another in so far that as pre-ignition persists, temperatures will rise and detonation will be accelerated.

Further, detonation in itself does not produce any very serious effects on the actual performance of the engine, but is chiefly objectionable due to the noise created. It probably has some effect of course on the wear and tear of the moving parts as extra forces are brought into play. Also, the formation of the aldehydes and tarry products of combustion will probably tend to gum up valves, piston rings, etc., and assist carbonisation. In the case of aero engines which are lightly built, detonation may have serious effects due to higher temperatures produced and increased stresses.

It is, however, the ambition of every oil refiner to produce a spirit which will not detonate in commercial vehicles. The modern methods of attaining this object are :—

(1) By keeping the volatility up, especially further up the distillation curve. This reduces the tendency to form a mist in the engine cylinder and therefore reduces the tendency to form the objectionable peroxides discussed before. As this desirability for high volatility clashes with the economics of refining when straight run spirits are made, it is obviously advantageous to attain it by the addition of natural gasoline. It is definitely known from practice that natural gasoline tends to improve the anti-knock properties of a petroleum spirit.

(2) By the use of cracked spirits. It can be shown that a fuel produced by the cracking (i.e., by the thermal decomposition) of heavier petroleum products contains unsaturated hydrocarbons other than the paraffin series which do not detonate at ordinary engine temperatures. The percentage of these present in the cracked spirit is as a rule sufficient to improve its anti-knock properties, but care has to be taken that gumming deposits are not produced in the engine.

(3) By the addition of definite quantities of spirits derived from other sources such as benzol, so that the temperature of initial combustion of the mixture is raised thus reducing its tendency to knock. This becomes a matter of economics, and very often places the refiner in the hands of other manufacturers. The amount of benzol required to have any effect on a knocking fuel under ordinary engine conditions varies from 10 to 30 per cent. Such large quantities as this cannot be manufactured in one place and an organisation is required to collect the spirit from the various gas works, coke ovens, etc., where benzol is produced.

(4) By the addition of dopes, the best known of which is tetra ethyl lead.

There was a good deal of doubt about the use of ethyl lead at first on account of its poisonous properties, but it has been definitely shown by a Commission appointed by the United States Govern-

ment that in the small quantities (about 4 c.c. per gallon) in which it is used in the fuel, no injurious results to the health of persons breathing the exhaust can be detected. Great care has to be taken of course in the manufacture of the compound, but this applies to many other substances in the Chemical Industry.

Of these four methods no doubt a combination of (1) and (2) with the addition of a small quantity of dope will solve the problem and both the engine manufacturers and the oil refiners are now fully alive to improvements which can be effected.

With regard to engine design the tendency to knock will be decreased by more efficient vaporisation in the carburettor, longer induction pipes to promote equilibrium, and cylinder heads designed to keep carbon formation down to a minimum. Increasing the ratio of compression increases the tendency to knock as discussed above, so that the benefits of higher efficiencies and power-weight ratios in this direction are limited by the fuel. Any means therefore of reducing knock will tend towards higher compressions and more efficient engines.

The knocking characteristics of a fuel are determined by using it in a variable compression engine and determining, under more or less standard conditions, the highest useful compression ratio (H.U.C.R.) which can be employed without knocking. Often, a standard non-detonating fuel is used as a basis for comparison.

In America it has been proposed to use as a standard fuel a mixture of pure normal heptane and tri-methylisobutyl octone. Both these spirits have practically the same physical characteristics. Their boiling points are the same (98° C.) and their gravities and viscosities are very similar. The former, however, has an extreme tendency to knock and the latter is practically similar to benzol in its anti-knock properties. By mixing these fuels in varying proportions therefore, various anti-knock values could be obtained, but constant conditions in the carburettor and induction pipe could be maintained.

Crank case dilution.—A further evil resulting from heavy non-volatile constituents in a motor spirit is that known as Crank Case Dilution. This is caused by the lubricating oil on the cylinder walls absorbing the heavier portions of the unvaporised fuel and thus reducing its own viscosity. The following table shows how an ordinary heavy gasoline will affect the viscosity of a lubricating oil.

	Viscosity at 100° F.
New oil ..	300 secs.
10% dilution ..	168 „
20% „ ..	115 „
30% „ ..	71 „
40% „ ..	44 „

This effect is more pronounced at starting when the engine is cold, as the less volatile constituents of the fuel are more in evidence in the liquid state in the cylinder, and also because when cold a lubricating oil will absorb more of them. As the engine warms up a state of equilibrium is reached, when the lubricating oil in the crank case gives off its absorbed constituents of the fuel through the crank case vent as fast as it absorbs them in the cylinders. Dilutions of 10 to 20 per cent. are not uncommon.

The remedies for this are :—

(1) Low and point fuels.
(2) Increased ease of starting and acceleration so that the engine warms up quickly.
(3) Continuous distillation of the lubricating oil in a small rectifier by using the heat of the exhaust. This method is now common in many American cars.

Purity of motor fuels.—From the point of view of operation in the engine, motor fuels should not contain any corrosive impurities. Sulphur is the one usually found in petroleum spirits, and refiners have given a good deal of thought to the removal of sulphur compounds. The chief troubles with sulphur in a motor spirit are :

(1) Corrosion of the copper or brass parts of the carburettor, including the feed pipes.
(2) Pitting of the exhaust valve by the formation of sulphurous acids after combustion.
(3) Objectionable smells both in the spirit and the exhaust.

In America, Government specifications allow 0·1 per cent. of sulphur in motor spirits, but this is considered excessive by many engine manufacturers. In England the market standard is 0·015 to 0·02 per cent.

Other ingredients of petroleum spirits such as aromatic unsaturated hydrocarbons were at one time considered as impurities, but their anti-knock properties have now rendered them highly desirable.

Fuels other than petroleum spirits.—A considerable amount of investigation has been carried out on alternative motor fuels with a view to anticipating a shortage of petroleum. The most promising of these is alcohol. Methyl alcohol can be produced by the destructive distillation of wood, vegetation, etc., or by passing carbon monoxide and hydrogen at about 330° F. over metallic nickel which acts as a catalyst. Methyl alcohol, however, is poisonous, which rules it out as a motor spirit.

Ethyl alcohol can be made by the action of sulphuric acid on the ethylenes in coke oven gas. Isopropyl alcohol is made in America from petroleum gases.

The chief features of alcohol as a motor fuel are :—

(1) Its low volatility.
(2) Its low calorific value.
(3) Its high temperature of initial combustion.

This means that alcohol is non-detonating.

It appears, therefore, that there is scope for a fuel consisting of alcohol mixed with a certain percentage of natural gasoline to increase its volatility and calorific value. Many tests have been made in this direction and it has been shown that engines can run up to a compression ratio of 7 to 1 on an alcohol-gasoline blend without detonating and on a reasonable fuel consumption. One trouble with alcohol is that it absorbs moisture which reduces its miscibility with gasoline.

Other fuels proposed are benzol, which we have already discussed in connection with its anti-knock properties, and various spirits to be obtained from the low temperature carbonisation of coal and the hydrogenation of coal (the Bergius process). Time and space forbid a discussion of these.

To conclude, it is obvious from the ground that has been covered that a very close liaison and exchange of views is required between the engine manufacturer and the oil refiner. The former should be equipped with up-to-date laboratories and should be *au fait* with all the chemical and physical side of the properties of fuels. The latter should have his own experimental engines and apparatus to obtain first hand information as to the suitability of his fuels for the engines demanded by the public. By this means the engine manufacturer is not penalised by lack of suitable fuels and the oil refiner does not suffer financial loss through having to market fuels for freak engines.

REVIEWS.

PETROLEUM DEVELOPMENT AND TECHNOLOGY IN 1926. American Institute of Mining and Metallurgical Engineers, New York, 1927.

This book contains the papers, together with the discussion, presented before the Petroleum Division of the A.I.M.E., at Tulsa, October 11–12th, 1926, and New York, February 15–17th, 1927.

The work is divided into eight parts, Production Engineering, Refining Technology, Transportation Engineering, Corrosion, Production, Petroleum, Economics, and Round Table Discussions on Petroleum Engineering, Educational Problems and on Petroleum Engineering Research Problems. Each part contains papers dealing with various aspects of the subject, with consequent discussions thereon, and the whole occupies 956 pages. This interesting book should prove invaluable to all petroleum technologists desirious of keeping in touch with the latest developments in the industry.

GEORGE SELL.

DIE GEWINNUNG VON ERDÖL. By G. Schneiders. Pp. 363. J. Springer, Berlin, 1927.

This is a book specially for mining engineers. The author, under the above title, adds, "with special consideration of the mining extraction."

Divided into three parts, "The Geology and Opening out of Oil Deposits" (Part I.) occupies twenty-two pages, whilst (Part II.) "The Extraction of Oil by Depth-Boring," is dismissed in some thirty pages, and then "The Extraction of Oil by Subterranean Mining" (Part III.) is treated at length, some 300 pages being devoted to this subject.

Passing at once to this section, the author deals with "Shafts," and their sinking, sub-division into compartments, lining, drainage and so forth, he then passes on to "Appliances Below Surface"—the driving of galleries or drifts, their timbering (wood, concrete, ferro-concrete, etc.) with description of certain boring appliances.

"Traction" is next described, and then the special modes applicable to the sands containing the oil which it is desired to exploit.

"Ventilation" is next dealt with, with a long chapter upon Fans. The "illumination" forms another section, and "Safety" matters are considered. Finally, the treatment of the crude oil (separation from sand, etc.) is described, and the book concludes with some remarks upon "Power Management" and an estimate of the profit obtainable by the mining process.

The "oil man" will find himself at sea without a very practical knowledge of the principles of mining engineering. Section XV. "Der Abban" will be of general interest, as it deals with the actual extraction, according to the actual conditions presented by the oil deposit treated. A useful and interesting book.

J. E. MARSHALL HALL

THE GEOLOGY OF THE ROSENDALE ANTICLINE. Memoir of the Geological Survey, England. By W. B. Wright, R. L. Sherlock, D. A. Wray, W. Lloyd, and L. H. Tonks. H.M. Stationery Office, 1927. 4s. 6d. net.

The memoir deals with the area covered by the Rochdale sheet (76) of the New Series One-inch map, and is divided into 11 chapters. The first consists

of an introduction dealing with the area as a whole, together with notes of previous work carried out on the district as far back as 1839.

Chapters 2-7 deal with the general and detailed stratrigraphy, and for the latter purpose, the area is subdivided into five sections, each dealing mainly with a separate structural feature. The district embraced in sheet 76 falls fairly naturally into seven physiographic divisions, and so dependent are these features on the geology, that it has been found most convenient to describe the ground by areas nearly coextensive with one or more of these divisions.

The tectonics of the district already referred to in the introduction are summarised in Chapter 8, and two sketch maps are given which show in generalised form the main variations in the dip and strike, and the principal lines of faulting.

Chapter 9 deals with palæontology, and shows a remarkable advance in the study of Gonistite faunas associated with the Culm phase of the Carboniferous.

The glacial geology and a description of recent deposits is given in Chapter 10, while in the concluding chapter the mineral products and water supply of the district are dealt with.

The subject matter of the memoir is remarkably well arranged, while the very numerous plates, sketch maps and diagrams greatly assist the reader to comprehend the highly detailed geological description of the area. The appendix comprises lists of geological papers referring to the Rochdale sheet, Geological survey photographs, and the more important quarries in sheet 76.

W. H. Thomas.

BOOKS RECEIVED.

Fuel for Motor Transport. Fourth Memorandum. Dept. Sci. and Industr. Research. H.M. Stationery Office. 9d. net.

This Memorandum summarises the work done by the Fuel Research Division of the Department of Scientific and Industrial Research on power alcohol production by fermentation processes. The first section reviews the possibilities of producing fuels within the Empire and explains the reasons for the investigations on tropical and semi-tropical grasses. The second and third parts describe the work on the production of the fuel, and the fourth part deals with suction gas producers using anthracite, coke and, more particularly, wood or charcoal for motor transport vehicles.